THE PRODUCTION OF METHANOL BY THE CONTROLLED OXIDATION OF METHANE AT HIGH PRESSURES

FINAL REPORT

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EXECUTIVE SUMMARY

This report presents a study of the controlled oxidation of methane to methanol by oxygen. The reaction was investigated at several temperatures, at pressures of 50 and 125 atmospheres at three oxygen levels 5, 10 and 20% for three flow rates at each level (5, 10 and 20s/reactor volume).

Two reaction systems were devised: (i) Monoflow system wherein the reactants (methane, oxygen, small amount nitrogen/were mixed in a single cylinder. (ii) Dual flow system where the reactants of methane/nitrogen and oxygen were delivered from separate supply cylinders to a small mixing chamber.

Reaction analysis was performed by Gas Chromatography and the data obtained expressed graphically in terms of the percent yield of oxidized carbon product against the parameters of percent oxygen in the reaction mixture and flow rate.

Yields of methanol of 80% were obtained at 450°C and 50 atm at the 5% oxygen level.

Material balances for the reactants and products were within 5-10% for carbon. The mono and dual-flow systems are compared.

Introduction

For over a century research workers have studied the oxidation of methane and other hydrocarbons in both static and flow systems at sub atmospheric and super atmospheric pressures.

Reserves of natural gas in Canada are high though direct utilisation of the gas as a power source is inconvenient for reasons of storage, handling and application. Conversion to a liquid fuel would obviate the problems of storage and handling. The most applicable liquid fuel obtainable from natural gas (and methane in general) is methanol which can be used as a direct substitute for gasoline. This can be achieved by the controlled oxidation of methane to methanol, i.e. conditions are such that further oxidation to higher oxidation state products would be limited.

The bulk of the methanol produced in Canada today is derived from natural gas via a two stage process involving the intermediate formation of synthesis gas.

$$CH_4(g) + H_2O(g) \xrightarrow[\text{heat}]{\text{Ni}} CO(g) + 2H_2(g) \qquad \Delta H^o = 206 \text{ kJ/mol}$$

This gas is catalytically converted to methanol in a manner similar to a Fischer-Tropsch synthesis (1)

$$CO(g) + 2H_2(g) \xrightarrow[50\text{-}100 \text{ atm}]{\text{catalyst}} CH_3OH(g) \qquad \Delta H^o = -90.7 \text{ kJ/mol}$$

Maximum efficiency of a 2000 tonne/day plant is predicted to be 70% using such a process to produce fuel grade methanol.

Direct conversion of methane to methanol would be both simple and more efficient energetically, than the above process, and as such would

$$CH_4(g) + 1/2\ O_2(g) \longrightarrow CH_3OH(l) \qquad \Delta H^o = -128.3 \text{ kJ}$$

be a more favourable method to meet todays demand (2). The potential of methanol as a chemical feedstock should not be underestimated. It has found a variety of application as a single carbon source, both as a fuel and in chemical production (3).

Previous Work

Pichler and Reder (4) were amongst the earliest workers to study the partial oxidation of methane to methanol under flow conditions. A reduction in the oxygen content from 10 to 0.6% effected an increase in methanol yield from 24 to 60% (based on consumed methane) at 100 atm and 500°C for a 10s reaction period.

Newitt and Szego (5) showed in their study of the slow oxidation of methane, at 50 atm and 430°C, that as much as 51% of the methane burnt was converted to methanol at high flow rates for a 3% oxygen mixture. Reduction in the flow caused further oxidation and a decrease in the formation of methanol. Increasing the oxygen content of the reaction mixture to 5% resulted in only a 29% yield of methanol at 410°C.

Wiezevich and Frolich (6) conducted their methane and natural gas oxidation experiments at 130 - 135 atm and at temperatures between 300 and 520°C. They found that for methane alone temperatures of around 500°C were required before measurable reaction took place whereas for methane, containing 2% ethane, and 3% oxygen, that methanol formed 29% of the liquid product at 300°C. They concluded that ethane sensitized the reaction. They also investigated the effect of metallic catalysts such as nickel, iron, aluminum, calcium, chromel and silver, which with the exception of nickel and iron, gave improved yields. In 1937 Boomer

and his students produced three significant papers dealing with the oxidation of methane at elevated pressures (7,8,9). They investigated the effects of temperature, pressure, oxygen concentration and flow rate on the reaction.

A copper lined reactor (volume 12 mL) was used throughout their investigations. Their results may be summarized in terms of the methanol yield expressed as a percentage of the carbon burned, as follows: (1) Effect of oxygen concentration: (8.7 and 4.9%) Decreasing the percent oxygen in the methane/oxygen reaction mixture improved the methanol yield, (2) Effect of pressure: Of the three pressure levels investigated at 141, 184, and 231 atm, 184 atm was found to be optimal for reaction mixtures containing less than 7% oxygen. Above 7% oxygen, the yield became independant of pressure, (3) Effect of temperature: The temperature was optimized at 450°C regardless of the pressure (184 or 231 atm) at low oxygen contents (4.4 and 4.9%). At 8.7% oxygen the optimum temperature was reduced to 390°C. The yield remained independent of pressure albeit considerably lower, (4) Effect of flow rate: The influence of flow rate was not significant over the range studied (0.6 - 1.1 litres min^{-1}) though there was a tendency for the yield to maximize at intermediate flows at the low oxygen level. Under these optimum conditions a 65% yield of methanol was recorded.

The maximum CH_3OH yield found in their experiments however, was 74% at the slightly higher temperature of 475°C and 3.2% oxygen. Evidently this slight increase in temperature and reduction in oxygen concentration favoured methanol at 184 atm, while the optimum conditions applied generally at both 184 and 231 atm. In conclusion, the

parameters affecting the yield of methanol the most are temperature and oxygen content of the reaction mixture.

Boomer and Naldrett (10) later made a systematic study of the effect that catalysts and their form had on the oxidation of methane. Previous work had shown the physical character of the catalyst to be important (9). Comparison of the catalysts was made under the optimum conditions described above, and their activities expressed in terms of methanol yield. Copper blocks were the most effective catalyst followed by nickel blocks. This order was reversed when these metals were used in the form of gauze. Both were more active than silver gauze, and zinc gauze was the least active. It was postulated that the activity of the catalyst was related to the ease with which it underwent reversible oxidation and reduction. Zinc could not be reduced under the experimental conditions studied. They proposed that catalysts in the form of gauze were less effective than blocks because of the associated greater free space in the reactor.

Monel wire was also investigated, to assess if a promotor effect (copper and nickel) existed. Certainly the wire was as effective as nickel, though its performance in block form was not studied.

Boomer emphasized that since the oxidized carbon product represented less than 5% of the reactant, that the process would only be commerically feasible using a recycling system.

Many other publications have appeared which deal with the oxidation of methane but concentrate on the reaction mechanism and are conducted at subatmospheric pressures or are carried out in static systems. This literature, which is of interest, though not directly relevant to the

work described in this paper, has been adequately described in a recent review article (11).

The foregoing indicates that the oxidation of methane under pressure and at low oxygen concentrations favours the production of methanol at temperatures around 450°C.

Catalysts are directly applicable to this reaction. Both heterogeneous metal surfaces and homogeneous higher hydrocarbons can be used.

This report details the work carried out this year (Mar. 83-84) in the study of the methane oxidation reaction with a view towards the commercial production of methanol as an alternative fuel. This has included an attempt to optimize methanol formation by observing the effect of the various operating parameters (pressure, temperature, residence time and CH_4/O_2 ratio) on the uncatalyzed gas phase reaction, before proceeding to study catalytic effects.

Preparation of feedstock

(i) Reactants mixed in a single supply cylinder (Mono-flow)

In order to realize feedstock pressures above those of conventional cylinders, initially a high pressure (5000 psig) aluminum cylinder was used to store the feedstock of methane and oxygen. This cylinder was designed to withstand cryogenic temperatures and facilitate being charged to high pressure (at room temperature) with feedstock. The addition of oxygen always followed that of the methane and never exceeded 20% of the total; thus all homogeneous mixtures remained outside the explosion limit.

Charging of the storage cylinder with the reactants was controlled (Figure 1) using a filling line constructed from brass fittings and

copper tubing. This line permitted filling of the storage cylinder from separate supply cylinders of CH_4 and O_2. The storage cylinder had an internal volume of 7.9 litres and the O_2 and CH_4 cylinders had internal volumes of 44 and 49 litres respectively. This ratio of cylinder capacities meant that if full supply tanks were used then the storage cylinder could be charged to 125 atm at 20% oxygen without resorting to the cryogenic facility.

The crude composition of the feedstock was estimated, during the filling process, by monitoring the change in cylinder pressure with the addition of the CH_4 and O_2 gases.

The filling line was evacuated prior to the addition of both CH_4 and O_2. A check valve prevented the backflow of the storage cylinder contents.

A quantitative determination of the feedstock composition, which on occasion included some N_2 to act as an internal standard, was carried out by G.C.

(ii) Reaction System

The reactor itself consisted of a 75 cm x 1.43 cm o.d. (i.d. = 0.4 cm) 316 stainless steel tube (Autoclave Engineers). Associated with the reactor tube were the input (prereactor) and output (postreactor) lines.

Input line - Mono-flow system

The input line was constructed entirely from brass fittings, rated to above 3000 psig (Figure 2(i)). The line consisted of a pressure gauge (USG 0-3000 psig), an adjustable in line relief valve (Circle

Seals 2300) with vent to atmosphere, and a pair of pressure transducers (Validyne DP15). The first transducer was equipped with a 0-200 psig diaphragm and operated in the differential mode. It measured the small pressure drop across a metering valve (Hoke 1315M4B) and acted as a flowmeter. The second transducer was equipped with a 0-3200 psig diaphragm which operated in the integral mode and measured the absolute pressure of the feed in the system. The output from the transducers was read directly from the Validyne Twin channel Digital Indicator (model CD223). Both channels were set to zero prior to calibration.

Calibration of Transducers

Both transducers were calibrated against a standard Heiss Bourdon gauge. Calibration involved the system being pressurized to (i) 200 psig for the low pressure (flow) transducer (Figure 3) and (ii) 1000 psig (limit of standard gauge) for the high pressure (absolute) transducer (Figure 4). The pressure in both cases was reduced in increments with the transducer readouts being compared with the values indicated by the Heiss gauge.

Standardization of Heiss Bourdon Gauge

The integrity of the Heiss Bourdon gauge was checked against primary standards (S.V.P. of CO_2 and propane at known temperatures). Pressure readings from the gauge were compared from those in tables (Handbook CRC)(12). The gauge differed by 1.5% over the range measured and was considered satisfactory (Figures 5(a,b)).

Use of the Mono flow system permitted many experiments (20 full runs, minimum of 3 runs in each) to be carried out successfully.

However, ignition of the CH_4/O_2 mixture in the supply cylinder after charging it to 125 atm at the 20% O_2 level demonstrated that this method was dangerous. Though the cylinder had been charged with the same mixture to the same pressure on a previous occasion it was clear that direct mixing of these reactants was very hazardous.

This incident prompted the development of a new system wherein the reactant gases would be stored separately and only allowed to come together immediately prior to the reactor in a small mixing chamber. The system was designed so that if ignition of the mixture should occur then (i) provision was made for the escape of the combustion gases (relief valve) and would be vented through a ½" copper pipe to the outside instead of to the laboratory, (ii) the flow of O_2 and CH_4 would be sealed off immediately (check valves), and (iii) the volume of the reactant mixture even under pressure would be relatively small.

iii) Dual Flow Reaction System

A dual flow system which permitted CH_4 and O_2 to be drawn from separate supply cyclinders and mixed in a small volume was constructed (Figure 6). This system provided for the adequate control of both reactant gases and the subsequent reaction to be studied at 450°C at pressures of 35,50 and 65 atm at a flow rate of 10s (reaction volume)$^{-1}$ (34 cm^3 min^{-1} at NTP).

Input line

Separate lines were constructed to control the pressure and flow of CH_4 and O_2 respectively. CH_4 and O_2 gas was supplied from conventional high pressure cylinders (Linde - Union Carbide). The delivery pressure

of each gas was controlled with reducing regulators fitted with a shutoff valve. Since both the delivery pressure of CH_4 and O_2 was to be the same the desired ratio of CH_4/O_2 would be attained by flow control.

Metering valves were incorporated into each line for this purpose. In the O_2 line this valve acted as a coarse flow controller and a Nupro metering valve with vernier adjustment was connected in series to provide the fine control required to set the O_2 flow.

The flow in each line was monitored by Validyne DP15 pressure transducers operating in the differential mode across a Hoke 1315B flow controller, which acted as a constriction to effect a small pressure drop. The transducer outputs were read from a Validyne digital indicator (model CD223). The CH_4 transducer was equipped with a 200 psig diaphragm and the O_2 transducer with a 20 psig diaphragm to give better sensitivity.

Following the flow controllers, each line was equipped with a shutoff toggle valve (Hoke PS490) just prior to a 1-way check valve and the mixing chamber. The mixing chamber was a ¼ NPT brass cross (CAJON). The gases would mix in the cross before passing onto the reactor. An adjustable safety relief valve (Nupro SS-4R 3A5) was fitted to the remaining branch of the mixing cross. This was set at a pressure of about 30 psig above the experimental operating pressure. Provision was made for the relief valve to vent to the outside atmosphere (through the laboratory wall), via a ½" i.d. copper pipe.

Reactor pressure was monitored by a 1000 psig Heiss Bourdon gauge. The sample loop was installed prior to the reactor to permit the sampling of the reactant mixture. This loop also allowed the system to

be evacuated. The reactor and the output line remained the same for both mono flow and dual flow input systems.

In order that the reactor could be purged after experimentation, a high pressure line carrying nitrogen gas from a supply cylinder was connected into the system between the relief valve and the mixing cross. The complete system was pressure tested with N_2 prior to calibration.

Calibration of the Apparatus

The apparatus was calibrated using separate supply cylinders of CH_4 and N_2. CH_4 was fed into the system initially to the required pressure. N_2 was then admitted to the system and the gas ratio adjusted to the desired values, by means of the metering valves on each line. The transducer constrictions were adjusted to attain a balance between pressure drop (so as not to interfere too much with the operating pressure) and transducer sensitivity to flow.

The coarse O_2 metering valve was set at about 1/15 of the aperture of the CH_4 metering valve to give the best overall control of gas mixtures (more precise control was obtained by adjustment of the fine metering valve in the O_2 line).

This system permitted mixtures from 150:1 to 3:1 CH_4/O_2 to pass through the system.

All reactant mixture compositions were determined by G.C. analysis.

Reactor

The chosen material for the reactor was stainless steel since it best satisfied both the criteria of suitability and relative inertness towards the reaction system.

The reaction tube was heated over 45 cm of its length by two tube furnaces acting in series (Figure 7). The first (400W, Electrical Heating Apparatus Co., variac controlled) heated a 10 cm length and the second (Lindberg, 800W tube furnace) the remaining 35 cm. Temperature control was adequate (±5°C) for a system of this kind and was monitored by iron-constantan thermocouples. Their hot junctions were inserted into preformed grooves of cylinderical aluminum spacers (2.5 cm o.d.) which closely fitted the reaction tube and their cold junctions were placed in ice. The balance emf was determined from a potentiometer (Guildline Instruments) and the corresponding temperature read from tables (12).

Output line - Mono and Dual Flow

The output line was made from 316 stainless steel to obviate corrosion and possible catalytic effects (Figure 2(ii)). The flow of the reaction products, and ultimately of the system was controlled by a single metering valve (Hoke 1315M4Y). A 2.5 m x 0.16 cm o.d. (0.04 cm i.d.) length of 316 stainless steel tubing was connected between the metering and gas sampling valves. This effectively reduced the high pressure product output to atmospheric. The gas sampling valve was constructed from stainless steel and consisted of two sample loops. The valve permitted both direct injection of the product sample into the G.C. and its collection.

To prevent condensation of products with high critical temperatures the output line was heated by a combination of a cylindrical heating element (ElectroHeat systems SK105), which heated the final 15 cm of the reaction tube, and electrothermal heating tape which heated the

remainder of the output line and gas sampling valve. The heating tape was insulated to effect a higher line temperature. The line was maintained at temperatures of 200°C and above. Condensation was never found to be a problem under these conditions in this study.

The temperatures of both the cylindrical heating element and T-piece prior to the metering valve were monitored with thermocouples.

The flow of output gas was measured with a soap bubble flowmeter (N.T.P.).

Experimental Procedure

The oxidation of CH_4 was studied as a function of the variables of temperature, pressure, CH_4/O_2 ratio, reactor length and flow rate.

(i) Method - Mono Flow (Single flow of premixed gas)

The feedstock was prepared as described above in the desired proportion of approximately 20:1, 10:1 or 5:1 CH_4/O_2. The storage cylinder was connected to the input line of the reaction system. For the 50 atm runs the cylinder was filled to 1000 psig and for the 125 atm runs it was filled to 2100 psig. The reaction system was evacuated up to the storage cylinder valve. The feedstock pressure was controlled by a high pressure regulator set to give a delivery pressure of about 100 psig above the respective operating pressures of 735 psig (50 atm) and 1837 psig (125 atm). The stop valve was opened and the system allowed to reach operating pressure. The metering valves were preset to positions to give the desired pressure and flow rate. These had been predetermined with N_2 gas. The system was maintained at operating

temperature and the pressure was allowed to stabilize. The gases were mixed in the cylinder by rolling the cylinder for a few hours before use. The differential and absolute pressure values were read from the Digital Transducer Indicator (CD223) and converted to psig/atm from the predetermined calibration curves (Figures 3,4). The required flow rate was obtained by adjusting the output line metering valve.

Once a steady state was achieved (10-15 minutes) analysis of the reaction products was begun. Each determination took 15-20 min and several were made at each reactor flow rate studied.

(ii) Method - Dual Flow

The operation of the dual flow system was based on the calibration data obtained using CH_4 and N_2 as 'reactants'. O_2 was now substituted for N_2.

The system was completely evacuated, through the sample loop (1 hour or overnight). All valves except the coarse controllers were opened. These were left at their predetermined settings.

The system was isolated from the vacuum line. The transducer readouts were set to zero and the CH_4 constriction set at about 0.65 (Vernier scale). Both shut off toggle valves had been opened to permit evacuation and they both remained open during the charging procedure. This meant that admission of the gases to the reactor was controlled by the check valves. Since CH_4 was admitted through its corresponding check valve (Circle Seals (5000 psig) 1 psig cracking pressure) first, backflow through the oxygen line was prevented by the O_2 check valve. The O_2 flow transducer was used to monitor for this possibility in case of check valve failure (which has occurred) during the CH_4 filling

process. Such a backflow was indicated by a negative transducer readout. CH_4 was admitted to the system by incrementally increasing the cylinder delivery pressure. As the operating pressure of CH_4 was approached the constriction pressure dropped. The system was left to stabilize. This procedure took about 75 minutes (approx. 60 minutes charging - approx. 15 minutes to stabilize).

The O_2 line was charged by increasing the delivery pressure of the supply cylinder to the point where a flow was registered by the transducer. This indicated that O_2 was slowly entering into the mixing cross through the check valve (Nupro (3000 psig) 1 psig cracking pressure). This slow 'bleeding in' process of O_2 into a stream of higher pressure CH_4 required the back pressure in the O_2 line to be high. The flow rate (rate of O_2 bleed) was determined by the coarse and fine metering valve settings. Typically the coarse valve was opened approximately 0.25 of a turn and the fine valve 0.01 turns. This procedure ensured a slow and controlled admission of O_2 to the reaction system.

The back pressure of O_2 decreased steadily as the flow stabilized and the delivery pressure was increased to its operating value (Time for procedure = 45 minutes).

The desired CH_4/O_2 ratio was obtained by adjustment of the fine metering valve in the O_2 line and monitoring of the reactant gas composition by G.C. analysis of samples taken from the sample loop (Time for procedure 30-45 minutes).

The exit gas flow rate was adjusted to the appropriate value. The reactor pressure, flow transducer readings and flow rate values were noted together with the reaction zone temperature.

Analysis

A Burrell KD gas chromatograph was used for the analysis of the product gas.

An 8' x 1/8" o.d. stainless steel column packed with Carbosieve SII/100-120 mesh permitted the resolution of a mixture of H_2, O_2, N_2, CO, CH_4, CO_2, C_2H_6 and higher hydrocarbons. An 8' x 1/8" o.d. stainless steel column packed with Neopentylglycol succinate (NPGS)(10%); on Firebrick allowed the resolution of O_2 or N_2, CO, CH_4, CO_2, C_2H_6, H_2O, HCHO, CH_3OH, HCO_2H and $CH_3CO_2CH_3$. With such wide ranges in boiling points both columns required temperature programming.

A 10' x 1/8" O.D. stainless steel column packed with Porapak S (80-100) was found to perform very satisfactorily in the quantitative detection of the condensable products. This column was found to be more efficient (narrower peaks) than the 10% NPGS on Firebrick column with the resolution of N_2 and CO marginally improved and was used later, in preference to the NPGS column. Two further packings were tried but found to be unsuitable in the resolution of the condensable products of water and methanol. The first of these was a short (1.5' x 1/8" o.d.) stainless steel column packed with Carbosieve SII (100-120) as used for the gas analysis above. The second was also packed with a carbon molecular sieve from a different manufacturer (Analabs) called Spherocarb (3' x 1/8" o.d., 80-100 mesh). Although the Spherocarb column afforded some improvement over the Carbosieve it was slight and both packings, albethey in short columns, were unable to elute methanol quantitatively and consequently were not used for the determination of water and methanol.

Helium was used as the carrier gas and a Burrell KD thermal conductivity cell for detection. The thermal conductivity cell was checked for linearity with gaseous and liquid mixtures of interest and found to be satisfactory.

This system allowed the trapping out and collection of any unidentified compounds which were compared with known compounds to determine their identity.

Compounds in amounts too small for detection by G.C. were collected and could be analyzed using alternative methods.

Material Balance

(i) Mono-flow system

A material balance was obtained for the reactants, CH_4 and O_2, at the 20:1 and 5:1 ratio levels at 125 atm. This was achieved by incorporating a small amount (1-3%) of N_2 into the reactant mixtures. The reactant carbon and oxygen to nitrogen ratios were determined after the reactant mixture had passed through the reaction system at subreaction temperature ($\ll$350°C). This procedure was adopted to obviate the changes in the reactant mixture that occur with increased temperature and pressure and permitted the best comparison between reactant/nitrogen and products/nitrogen. In retrospect the CH_4/N_2 and O_2/N_2 ratios should have been determined at ambient temperature since some O_2 seemed to have disappeared at this temperature of 350°C.

The material balances may be presented as:

I. carbon balance $$\frac{CH_4}{N_2} R = \frac{CH_4}{N_2} P + \frac{CO}{N_2} + \frac{CO_2}{N_2} + \frac{CH_3OH}{N_2}$$

II. O_2 balance $$\frac{O_2}{N_2} R = \frac{O_2}{N_2} P + \frac{CO_2}{N_2} + \frac{1}{2N_2} \{CO + H_2O + CH_3OH\}$$

The $\frac{O_2}{N_2}P$ term was zero in all cases, i.e. O_2 was completely consumed.

The ratios in the above equations were obtained directly from the peak areas recorded on the chromatogram. The carbon to nitrogen and oxygen to nitrogen ratios before reaction were compared with the total carbon in the products relative to nitrogen and total oxygen relative to nitrogen in the products (Tables 1 and 2). The carbon balance was good (within 5-10%) but the oxygen balance indicated that oxygen was being consumed by oxidative processes other than those involving CH_4.

(ii) Internal Standard - Dual Flow System

Nitrogen was chosen as the internal standard and added to the CH_4 supply cylinder at the 2% level. This would enable both carbon and oxygen balances to be determined.

Determination of O_2 Consumption by Reactor Wall

(i) 50 atm

Medical air at a pressure of 50 atm was allowed to flow through the reactor at 450°C and its composition at the exit analysed.

This procedure was carried out before and after the reactor was cleaned (cf. pg.24). The results show that O_2 loss to surface oxidation was about 0.7% of the air passing through the reactor prior to its cleaning (Table 3). Once cleaned loss of O_2 could not be detected (Table 4).

This result was to be expected and O_2 consumption by surface processes will increase with operation of the reactor.

The pressure and temperature were varied to determine their effect on O_2 concentration. Pressure (0-50 atm) had a lesser effect compared

to temperature, where the O_2 concentration decreased with increase in temperature.

(ii) 125 atm

Although not determined directly, increasing the reactant pressure in the mono flow system reduced the yields of useful products particularly at the lowest O_2 concentration of 5%. By implication oxidative processes at the reactor wall would seem to have been promoted by increase in pressure. This was borne out by the oxygen balance, as discussed below.

Oxygen balance

The products of the reaction showed a surplus of O_2 over that determined in the reactant gas (Tables 1 and 2) at 125 atm. Oxygen was clearly being consumed even at subreactive temperatures (used to determine O_2/N_2 reactants), most likely by the walls of the reactor. During reaction however, this oxygen was competitively stripped from the walls of the stainless steel reactor and incorporated into the oxidation products. Interestingly the oxygen imbalance was larger at the higher O_2 level (6.2:1), indicating that the amount of O_2 combining with the wall (when determining the O_2/N_2 reactant ratio) was greater, and reflected in the product O_2/N_2 term.

The yield of methanol was at its highest at this O_2 level (6.2:1) (Figure 9). A reaction system wherein the methoxy radical was formed in part by the competitive reaction of the methyl radical with surface oxides, which then abstracts a hydrogen atom from CH_4 to form methanol, would be consistent with the above observations.

At 50 atm the position was reversed with more CH_3OH being formed at the lowest O_2 concentration.

Since O_2 consumption by the reactor wall was neglible at 50 atm then all of the available O_2 at the 5% level was consumed in the oxidation of CH_4. It would appear that while low O_2 concentrations (5%) favour CH_3OH production that all of this O_2 is needed by the CH_4 oxidation reaction in order to produce CH_3OH in good yield.

Results* & Discussion

(i) Mono-flow system

CO and CO_2 were produced in small quantities at 350°C using the 10 cm reactor length. At 450°C their yield improved to 1% of the total input carbon. Increasing the reactor length to 45 cm brought about the additional formation of CH_3OH and H_2O. These products were eluted from the column in the order: CO, CO_2, H_2O and CH_3OH (see Figure 8).

Ethane, which was eluted after CO_2, was also detected, with the oxygen concentration at 10% and 20% at 50 atm and at all oxygen concentrations at 125 atm.

The products were quantified in three ways: (i) as a percentage of the total product mixture (including unreacted CH_4), (ii) as a percentage of the input carbon and (iii) oxidized carbon products as a percentage of the total oxidized carbon or carbon burned. This latter parameter was the most significant and will be used in the following discussion.

*Tables of Experimental Data are appended (Appendix A).

The production of methanol maximized at 81% at 50 atm. The highest value obtained at 125 atm was 65%. Clearly pressure did not have the anticipated effect (increased yields) based on previous work (9).

Effect of O_2 Concentration

CH_3OH (Figure 9)

(a) 50 atm

The highest methanol yield (81%) was obtained at the lowest oxygen concentration of 5%. The yield became independent of oxygen at the 10% and 20% levels and more importantly falls to less than half the value (30%) obtained at the 5% level.

(b) 125 atm

The yield increased from around 40-60% with increase in oxygen concentration (5-14%). The reaction would seem to be influenced by increased oxygen at higher pressures. However, this trend is complicated by the possibility that the oxygen consumed may not have been totally converted to oxidized product, and that some may have been reacting with the reactor wall in other oxidative processes. This possibility will be discussed more fully later. It is sufficient to say that if this was occurring then the effect on the yield would be less severe at the higher oxygen concentrations.

CO (Figure 10) (a) 50 atm

The yield of CO was low at the 5% O_2 level and remained steady at around 30% at the 10% and 20% levels.

(b) 125 atm

CO decreased almost linearly with increase in O_2 concentration.

CO_2 (Figure 11) (a) 50 atm

The yield pattern of CO_2 is similar to that of CO at 50 atm.

(b) 125 atm

CO_2 decreased, as the CO decreased at 125 atm, to the 10% oxygen level but was not influenced much further by increasing O_2.

The change in CO_2 production paralleled that of CO which indicated that it was formed by the oxidation of CO. CO production fell with increased CH_3OH and vice-versa. At 50 atm and 5% O_2 the partial oxidation clearly favoured CH_3OH whereas at 125 atm, CO and CO_2 levels were at their highest. The increased pressure would seem to favour more complete oxidation of CH_4 to CO and certainly would be expected to favour the gas phase production of CO_2 from CO. Both CO and CO_2 diminish with increasing O_2 concentration at 125 atm.

Effect of flow rate

CH_3OH (Figure 12)

The CH_3OH yield at 50 atm was reasonably independent of flow rate while at 125 atm it was favoured overall by an increase in flow. Preservation of CH_3OH would be expected as the reaction residence time was reduced.

CO (Figure 13)

At 50 atm the CO yield tended to increase with increasing flow rate while at 125 atm the reverse was true.

CO_2 (Figure 14)

Yield of CO_2 generally decreased with increase in flow rate regardless of pressure.

At 50 atm the production of CH_3OH was independant of flow rate and CO and CO_2 were the only yields effected. Preservation of CO was favoured by higher flow rate, i.e. short residence times which caused a reduction in the yield of CO_2.

At 125 atm the survival of CH_3OH was improved at higher flow rates and consequently both CO and CO_2 yields fell.

HCHO (Table 5)

Formaldehyde was formed in very low quantities (~0.001 % of carbon burnt) and was not detected by G.C. (Pararosaniline method). This low level indicated that the extent of oxidation of CH_4 to liquid products was restricted to CH_3OH.

C_2H_6

Ethane was detected at 50 atm at the highest O_2 concentration of 20% alone. It was detected at all O_2 concentrations at 125 atm though not in significantly higher amounts than at 50 atm. The amounts detected (1%) were small but consistently produced. This indicated the presence of methyl radicals in the gas phase which were combining to form ethane when O_2 had been completely consumed

and indicated that CH_3OH formation had reached a limit.

(ii) Dual Flow System

Operating at 450°C, 50 atm and around 10s reac. vol^{-1}, reaction first became significant at a CH_4/O_2 ratio of 30:1 as indicated by the production of CO. H_2O was produced in larger amounts as the concentration of O_2 was increased. The Porapak S column was superior to the 10% NPGS column in handling these amounts. CH_3OH, however, was produced in low yield, typically 7-14% of the total oxidized carbon (Table 6a)).

The effect of increasing the O_2 content of the reactant gas was negligible with regard to CH_3OH yield, though yields of CO and CO_2 did increase correspondingly. The reactant O_2 was completely consumed by the reaction, i.e. none was detected in the exit gas.

At this point the reactor was dismantled and thoroughly cleaned with abrasive powders. Considerable amounts of iron oxides had built up in the reactor and a sample of these which included magnetite (Fe_3O_4) was kept. The reactor tube was flushed out with isopropyl alcohol and the washings kept for analysis. It was thought that considerable O_2 was being consumed by oxidation processes at the reactor wall having a detrimental effect on CH_3OH yield.

No improvement in CH_3OH yield was effected by this procedure over the CH_4/O_2 range of 20:1 - 10:1. The amount of H_2O produced by reaction did decrease however.

The reactor was again dismantled and some Apiezon L grease, in chloroform, was applied to the reaction zone. It was considered that

reaction activity with respect to CH_3OH may have been aided by initial hydrocarbons on the reactor wall.

It was presumed that the reactor tube had been lightly coated with some oil or antioxidant prior to despatch. It was hoped to imitate this condition with the Apiezon, assuming that the original hydrocarbons had been removed by reaction at the wall. This layer may have been responsible for supplying $H^{\cdot}$ to combine with $CH_3O^{\cdot}$ radicals.

No improvement in CH_3OH yield was observed.

The major difference between the mono and dual flow systems lay in the method by which the reactants were mixed, and this more importantly affected the extent to which they mixed. The reactant gases, in the monoflow method, were mixed directly in the supply cylinder which was repeatedly rolled to improve mixing and left on its side for between 24 and 72 hours. This procedure assured intimate mixing of the contents. However, in the dual flow method the reactant gases first came into contact with each other in the small mixing cross (int. vol 0.140 ml) and passed through the short prereactor section (int. vol. 0.3 ml) to enter the 45 cm heated reaction zone. Mixing of the gases at 50 atm in such a small volume was far inferior to that achieved in the supply cylinder. It is considered that the flow in the mixing cross and prereactor is laminar in nature with the O_2 forming a narrow homogeneous stream (see figure 15(a)) within the general flow. The O_2 has little chance of becoming dispersed throughout the reactant stream prior to reaching the reactor zone.

CH_3OH is nevertheless produced, albeit in small quantities, while the 'final' products of the CH_4 oxidation are formed in high yield. The reactant O_2 was completely consumed by the reaction (i.e. none present

in the exhaust gas) and C_2H_6 was detected showing an excess of CH_3 radicals, i.e. the reaction limit.

In view of these results it can be postulated that the CH_4 is being oxidized initially to CH_3OH which is further oxidized, at the periphery of the O_2 stream, i.e. in an O_2 rich environment, and that the CH_3OH produced in the less rich O_2 regions in the reaction cross section is small (Figure 15(b)).

It is clear that the reactants need to be intimately mixed in order to benefit from controlled oxidation using low O_2 concentrations. This was recognised by Boomer and his student (13).

The situation called for more turbulent flow of the reactants to achieve good mixing.

To this end the mixing cross was packed with stainless steel wool and a double twined length of stainless steel capillary tube was inserted into the prereactor section of the reactor tube.

This effected a definite increase in the CH_3OH yield improving the value expressed in terms of total oxidized carbon from 14 to 33% (Table 6b)).

Unfortunately the steel wool destabilized the reaction mixture causing it to ignite. The associated increase in pressure caused the relief valve to open at its preset value and the system lost pressure completely. Both the CH_4 and O_2 lines were closed at their respective toggle valve shutoff points. The small reaction volume enabled the ignition to be kept under control, i.e. confined to the reaction and relief valve exhaust-systems.

The sealing O-ring on the O_2 line check valve was damaged causing it to fail and the back pressure buckled the O_2 transducer diaphragm

further down the line. This must have happened prior to the O_2 line being shutoff. The CH_4 check valve was undamaged and had operated correctly. The respective check valves came from different manufacturers. The Circle Seals supplied model was constructed to give better protection to its seals and to withstand a higher backpressure. For future experimentation the O_2 line will also be equipped with one of these check valves.

Assuming that the reaction mixture had approached the upper explosion limit at 50 atm (CH_4:O_2 = 7:1) then a source of ignition would still be required. It was concluded that the stainless steel wool effected the ignition by acting as an active surface, as had been found previously (13).

Clearly a non-reactive surface was required to achieve the necessary mixing. Teflon was chosen for this purpose. Teflon turnings were packed into the mixing cross and a double twisted strand of the same material was inserted into the prereactor section. Discs of porous polyethylene were cut and inserted into brass fittings which followed the check valves and were connected into the mixing cross. These discs would act as filters breaking up the laminar flow and effect a turbulence of the CH_4 and O_2 gases causing them to interdiffuse and hence achieve a good degree of reactant mixing.

Although mixing of the reactant gases was improved it was still, on analysis, as much as 50% less at the inlet than that at the outlet of the reactor, i.e. the amount of oxygen in methane determined at the input sample loop was one half of that sampled at the reactor exit when the gases were completely mixed.

The degree of mixing of the gases was improved with the insertion of a vernier needle valve (Aerosmith V54-2-11) into the input line between the mixing cross and the Heiss Bourdon gauge and sample loop tee. This measure improved the degree of mixing (% oxygen in methane measured at inlet to that measured at outlet) to 85%.

The yield of CH_3OH at 450°C and 50 atm (5% O_2 in CH_4) improved to 50% following this measure.

It now seems clear that the oxidised yields, and CH_3OH in particular, depend on the degree of mixing of the reactant gases. The more intimately they can be mixed the better the yields. This factor may well account for the variations particularly in CH_3OH yields reported in the literature.

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Table 1. Material balance for O_2 and carbon: Reactants and Products (Mono-flow system).

P = 125 atm T = 450°C L = 45 cm CH_4/O_2 = 6.2:1

Flow = 20s (reac. vol)$^{-1}$

$\frac{O_2}{N_2}$ reactants	$\frac{CH_4}{N_2}$ reactants	$\frac{CH_4}{N_2}$ products	$\frac{C}{N_2}$ products*	$\frac{O_2}{N_2}$ products*
5.355	38.12	31.43	38.60	8.9
"	41.40	33.33	41.46	10.2
"	40.27	33.70	43.41	10.5
"	38.28	30.70	38.19	8.1
"	41.59	34.0	44.70	16.8
"	38.74	31.32	37.49	4.4

*values obtained from 6 determinations made in Run 17.

Table 2. CH_4/O_2 = 18.7:1 other parameters as Table 1

3.50	92.63	64.5	70.14$^+$	6.2$^+$
"	86.57	91.75	95.65	4.1
"	92.63	89.5	93.75	2.81
"	85.88	84.60	88.40	3.86

$^+$values obtained from 4 determinations made in Run 18.

Table 3. Determination of % 0_2 in air after passing through reactor.

Pressure = 50 atm

Reactor Temp. (°C)	Air Flow ($cm^3 min^{-1}$)	$\%0_2$ in air	Ave $\%0_2$
454	70	17.60	17.92±0.24
	66	17.84	
	66	18.00	
	66	18.27	
450	33	17.97	18.04±0.5
	33	18.61	
	33	17.30	
	33	18.30	
449	17.7	17.06	17.67±0.4
	13.3	18.11	
	17.1	17.66	
	16.2	17.85	
18	40	18.44	18.52±0.24
	40	18.83	
	40	18.18	
	40	18.65	
P = 21 atm			
18	7.5	18.30	18.02
		17.75	
P = 3.5 atm			
18.5	80	18.61	18.65
		18.70	

b) Determination of 0_2 concentration in Medical air at NTP. 1 cm^3 sample size. Mean % 0_2 = 18.33±0.16.

Table 4. Determination of O_2 concentration in Medical Air after reactor had been cleaned.

P = 50 atm Temperature = 453°C Flow Rate = 40 cm^3 min^{-1}

$\%O_2(1) = 18.14 \pm 0.31$

$\%O_2(2) = 17.90$ 1 0.18

%0 determined at NTP = 17.85 ± 0.27

Table 5. Determination of HCHO concentration in product sample by Pararosaniline method.

Sample collected directly from G.C. outlet (1 cm^3 gaseous sample in 25 cm^3 water).

Absorbance	Average Abs.	HCHO (ppm)	yield % C burnt	$CH_4:O_2$
0.105 0.102 0.101	0.103	0.019	1.05×10^{-4}	10:1
0.295 0.293 0.293	0.294	0.054	3.0×10^{-4}	20:1

Table 6. a) Reaction product analysis - Dual flow system

Reactor temp. = 453°C Pressure = 50 atm

CH_4/O_2 = 16.6:1 Flow Rate = 10s (reac. vol)$^{-1}$

Run 21

Compound	CO	CH_4	CO_2	C_2H_6	H_2O	CH_3OH
%total	3.9	83.30	2.74	v.s.	10.50	0.50
%C in	4.3	92.12	3.03		9.6	0.55
%C burnt	54.5		38.46			7.05

CH_4/O_2 = 11.76:1 Flow Rate = 10s (reac. vol)$^{-1}$

Compound	CO	CH_4	CO_2	C_2H_6	H_2O	CH_3OH
%total	4.0	74.52	4.75	-	16.15	0.57
%C in	4.76	88.88	5.66			0.68
%C burnt	42.85		51.02			6.12

CH_2/O_2 = 10.26:1 Flow Rate = 10s (reac. vol)$^{-1}$

(i)

Compound	CO	CH_4	CO_2	C_2H_6	H_2O	CH_3OH
%total	2.36	76.36	4.91	-	15.82	0.54
%C in	2.81	90.70	5.83			0.64
%C burnt	30.23		62.30			7.0

(ii)

%total	3.96	73.35	3.72	v.s.	17.7	1.23
%C in	4.82	89.15	4.51			1.50
%C burnt	44.44		41.66			13.88

Table 6(b) Reaction product analysis - Dual flow system (mixing cross packed with steel wool).

Reactor temp = 457°C Pressure = 50 atm

CH_4/O_2 = 9.3:1 Flow Rate = 20s (reac. vol)$^{-1}$

Compound	CO	CH_4	CO_2	C_2H_6	H_2O	CH_3OH
%total	1.72	54.4	3.22	0.35	37.5	2.68
% C in	2.75	87.20	5.16	0.57		4.30
% C burnt	21.52		40.35	4.5		33.63

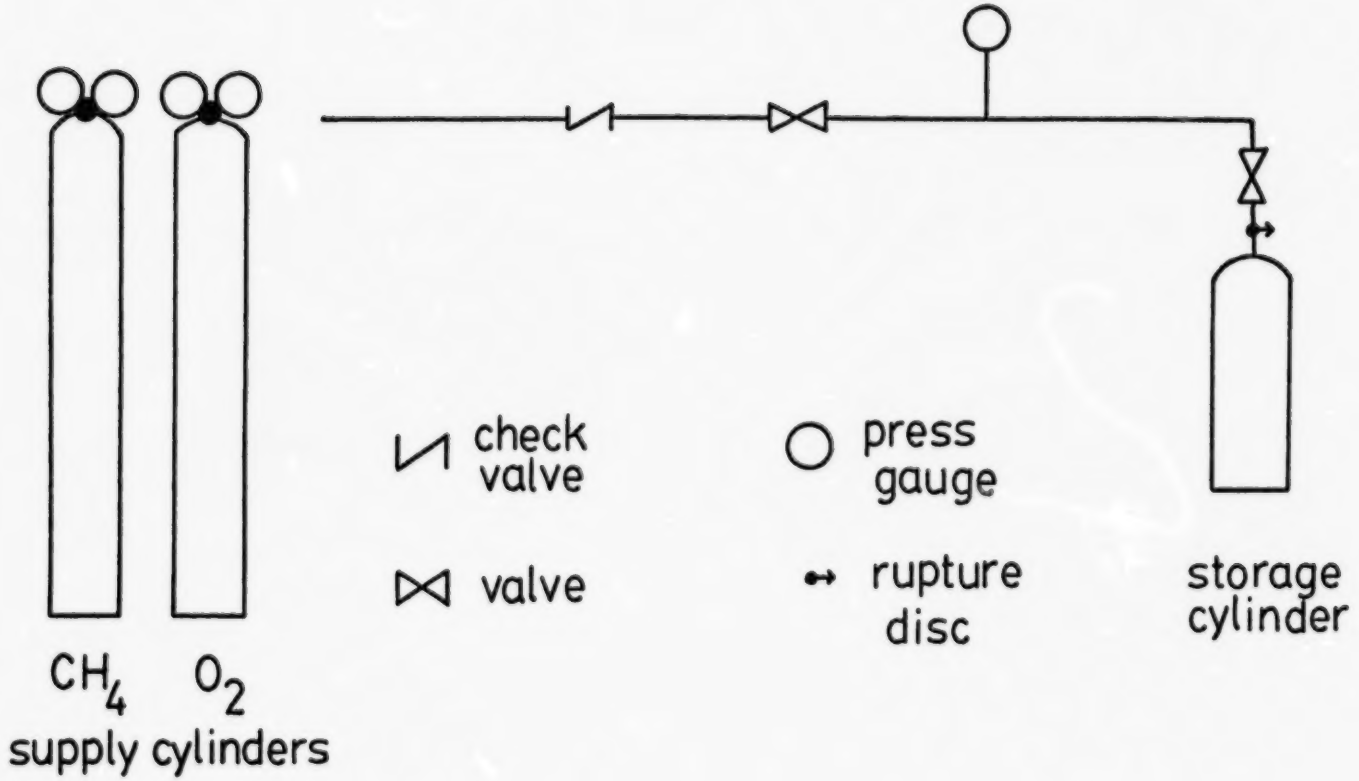


Figure 1. Filling line:- Mono-flow system

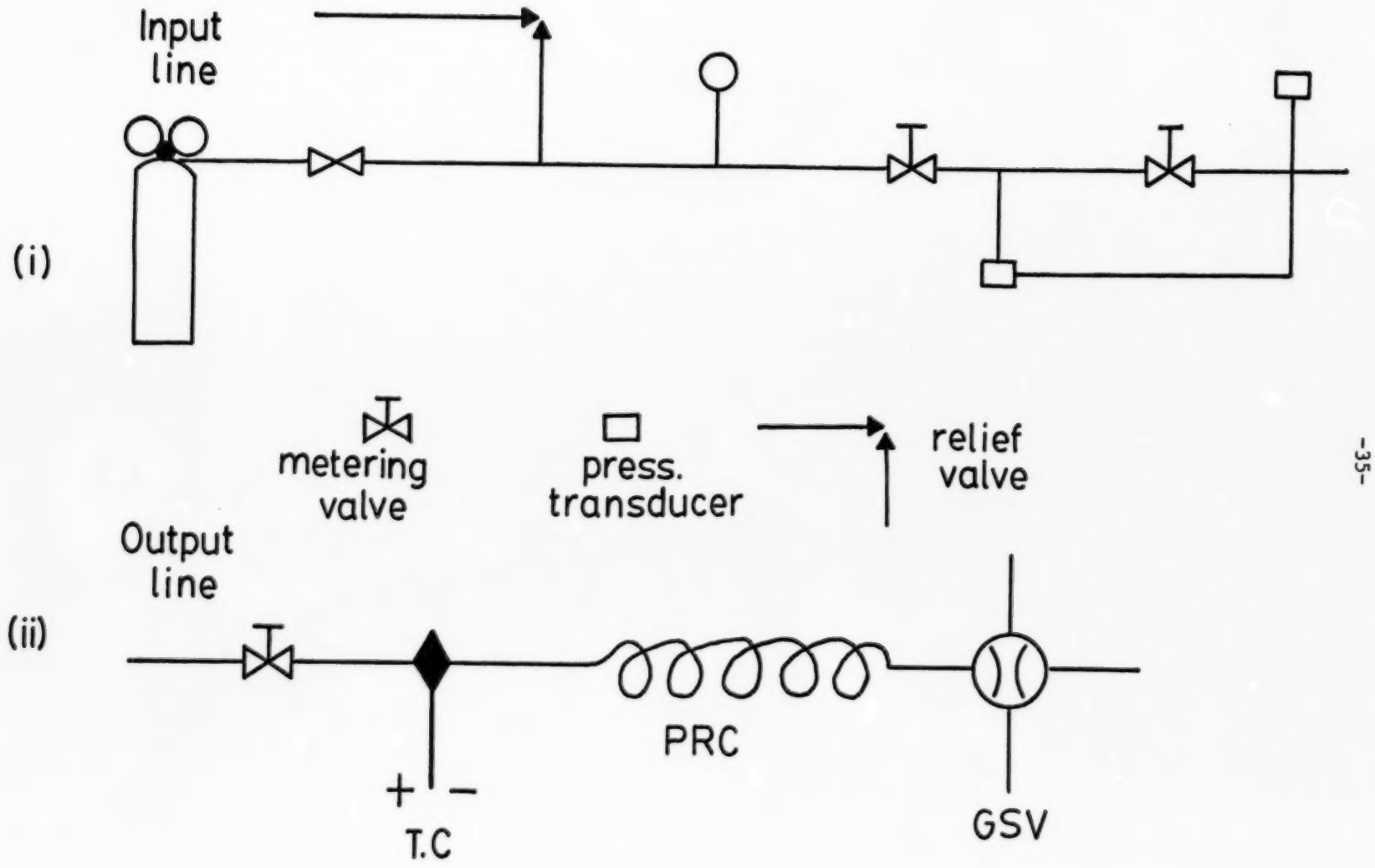


Figure 2. (i) Input line - Mono-flow system (ii) Output line-Mono and Dual flow systems.

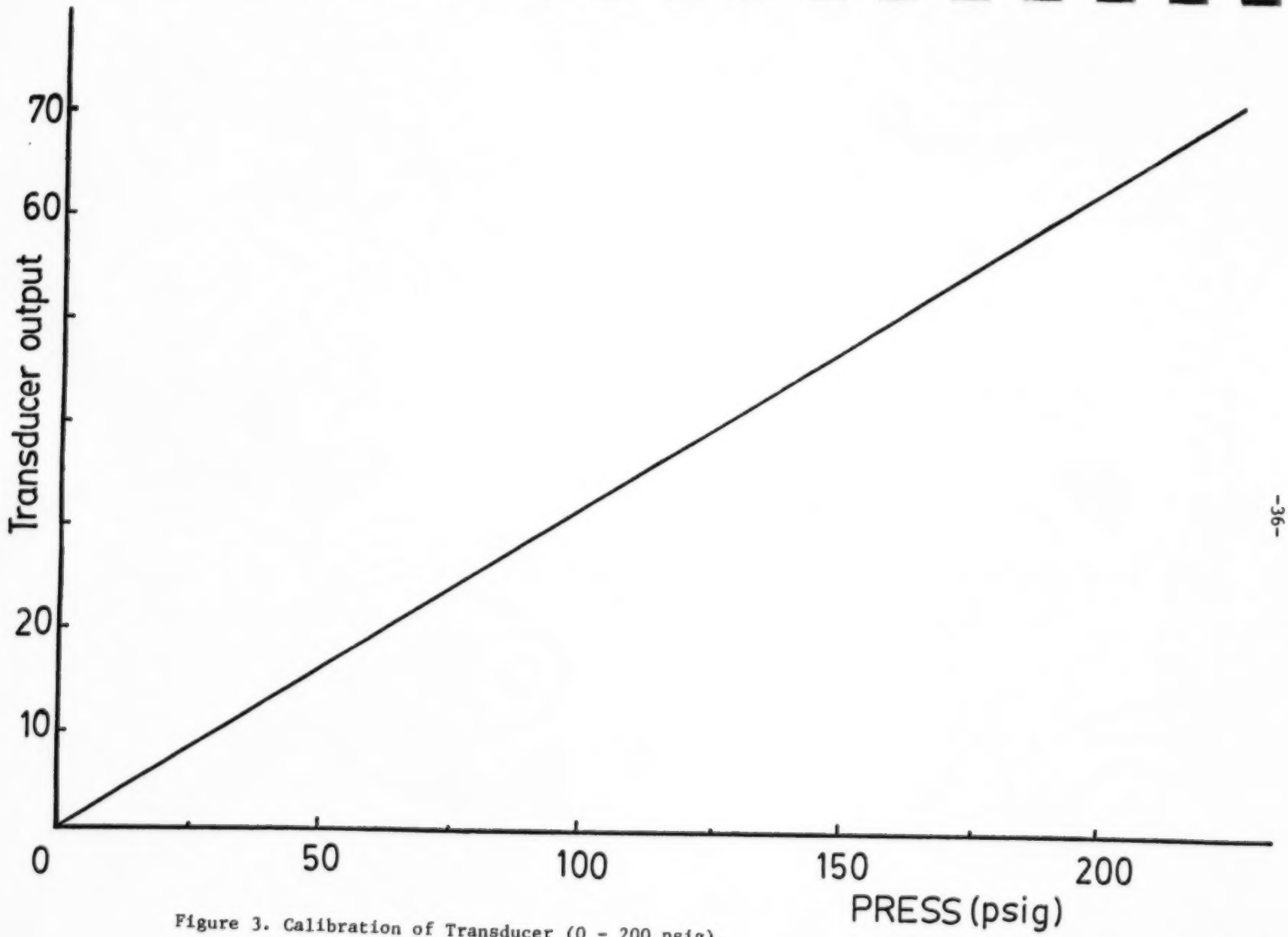


Figure 3. Calibration of Transducer (0 - 200 psig).

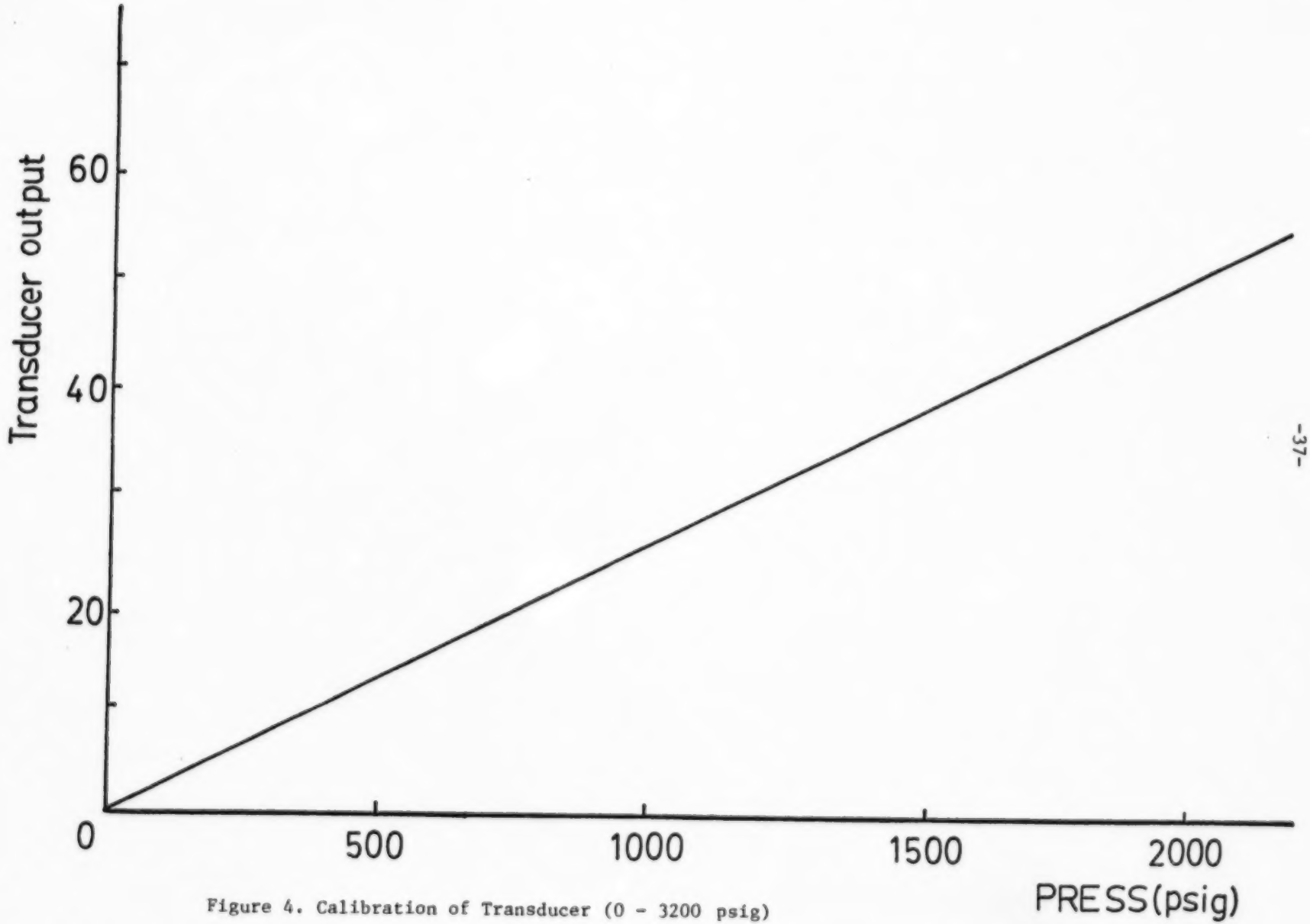


Figure 4. Calibration of Transducer (0 - 3200 psig)

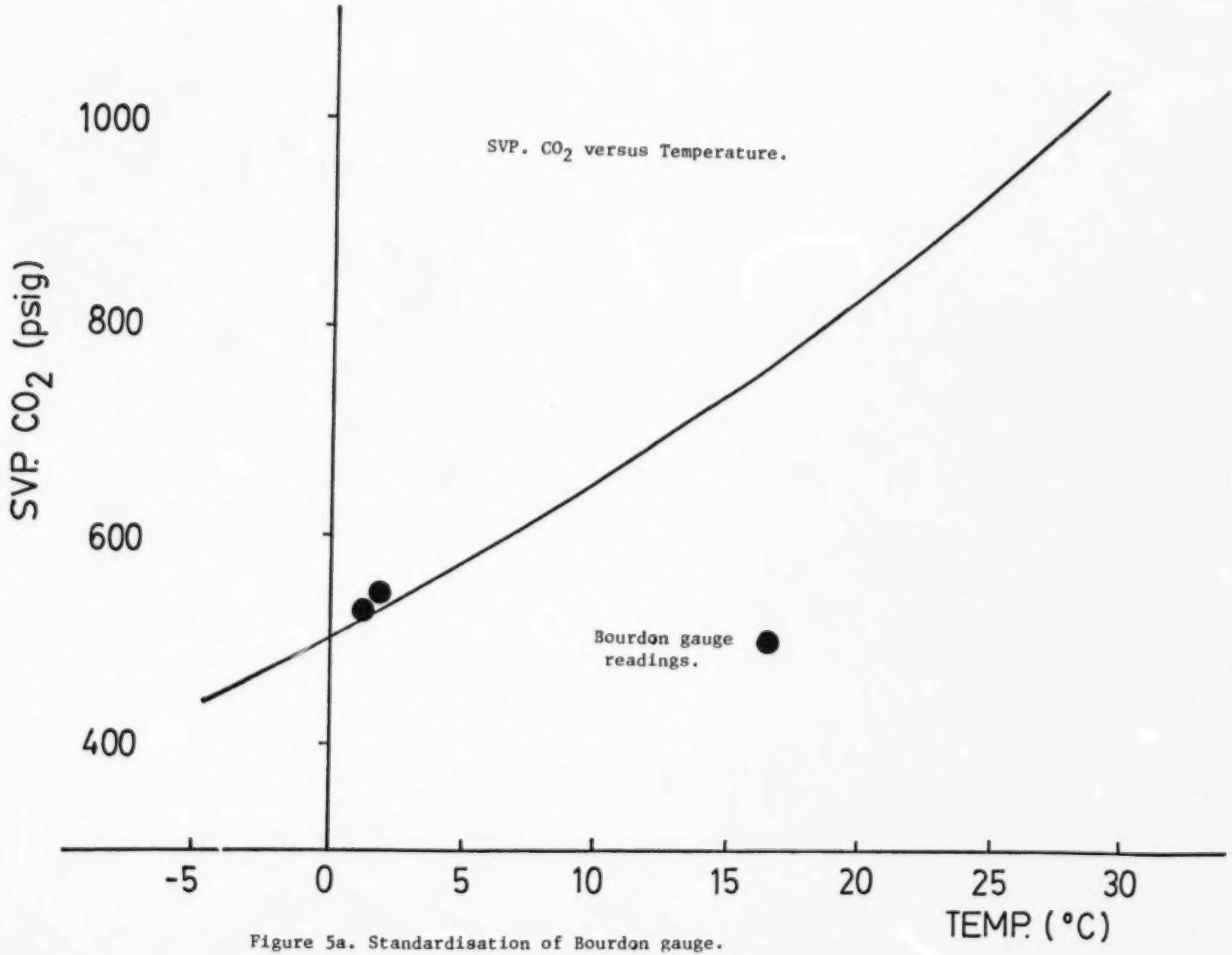


Figure 5a. Standardisation of Bourdon gauge.

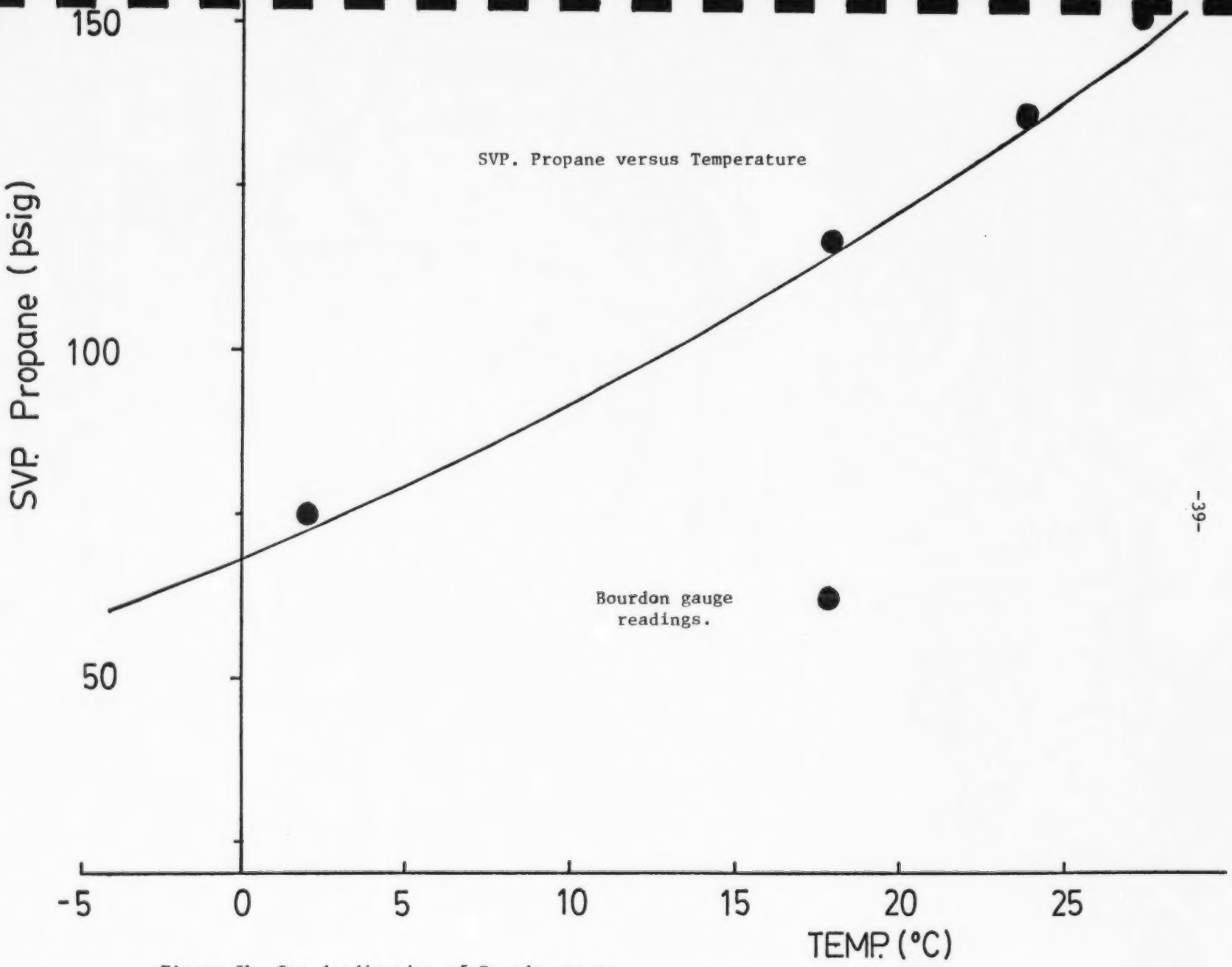


Figure 5b. Standardisation of Bourdon gauge.

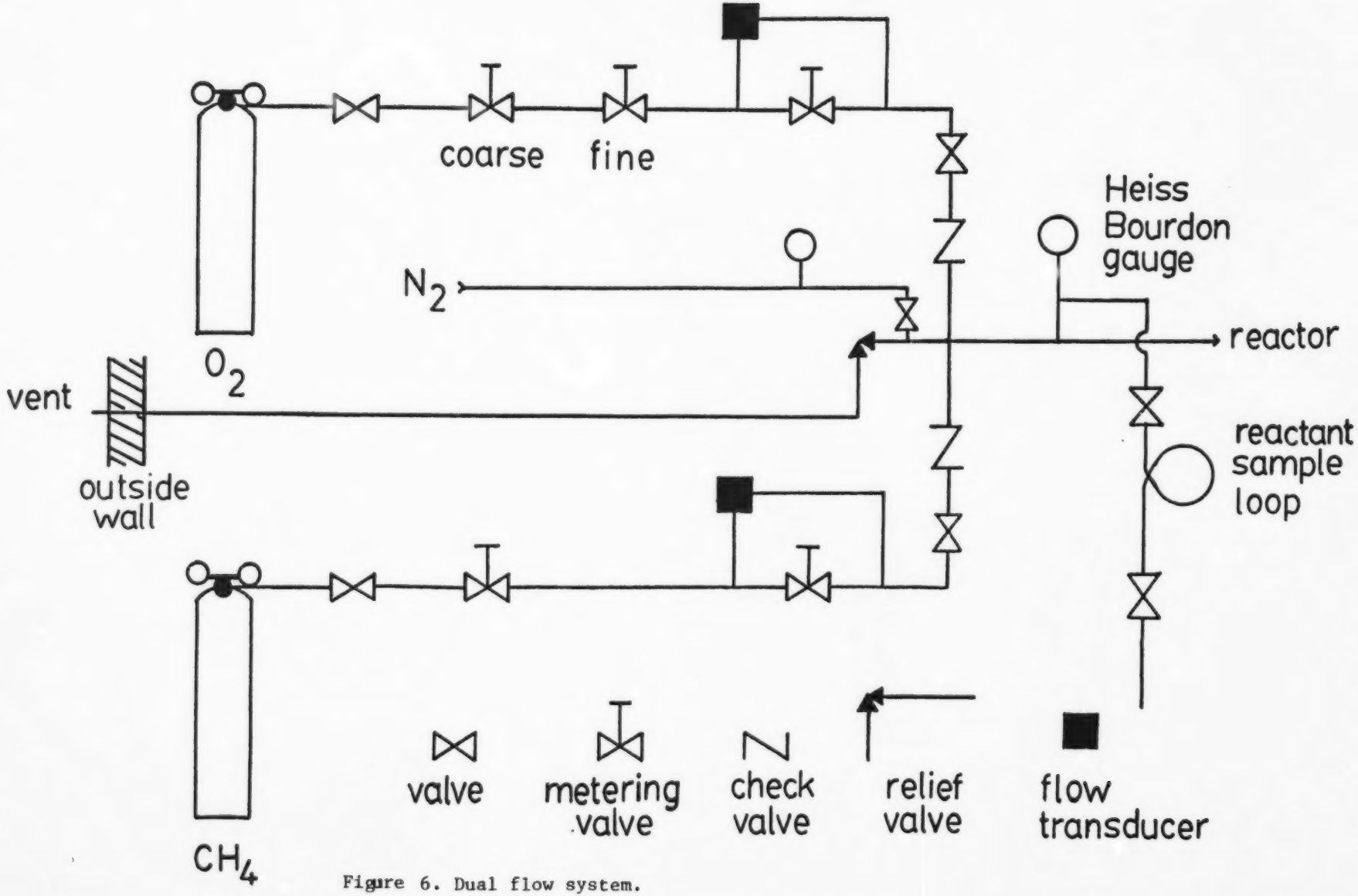


Figure 6. Dual flow system.

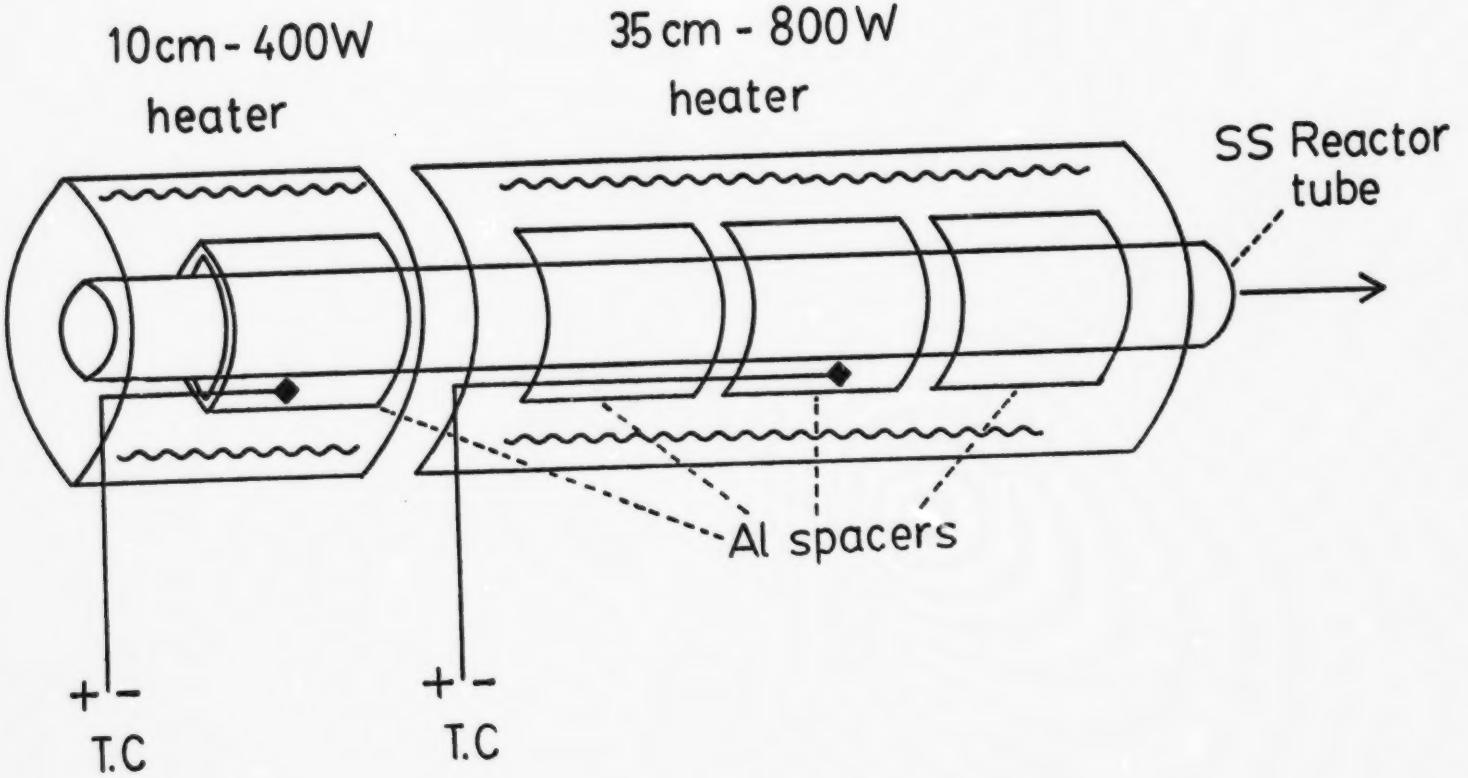


Figure 7. Reactor

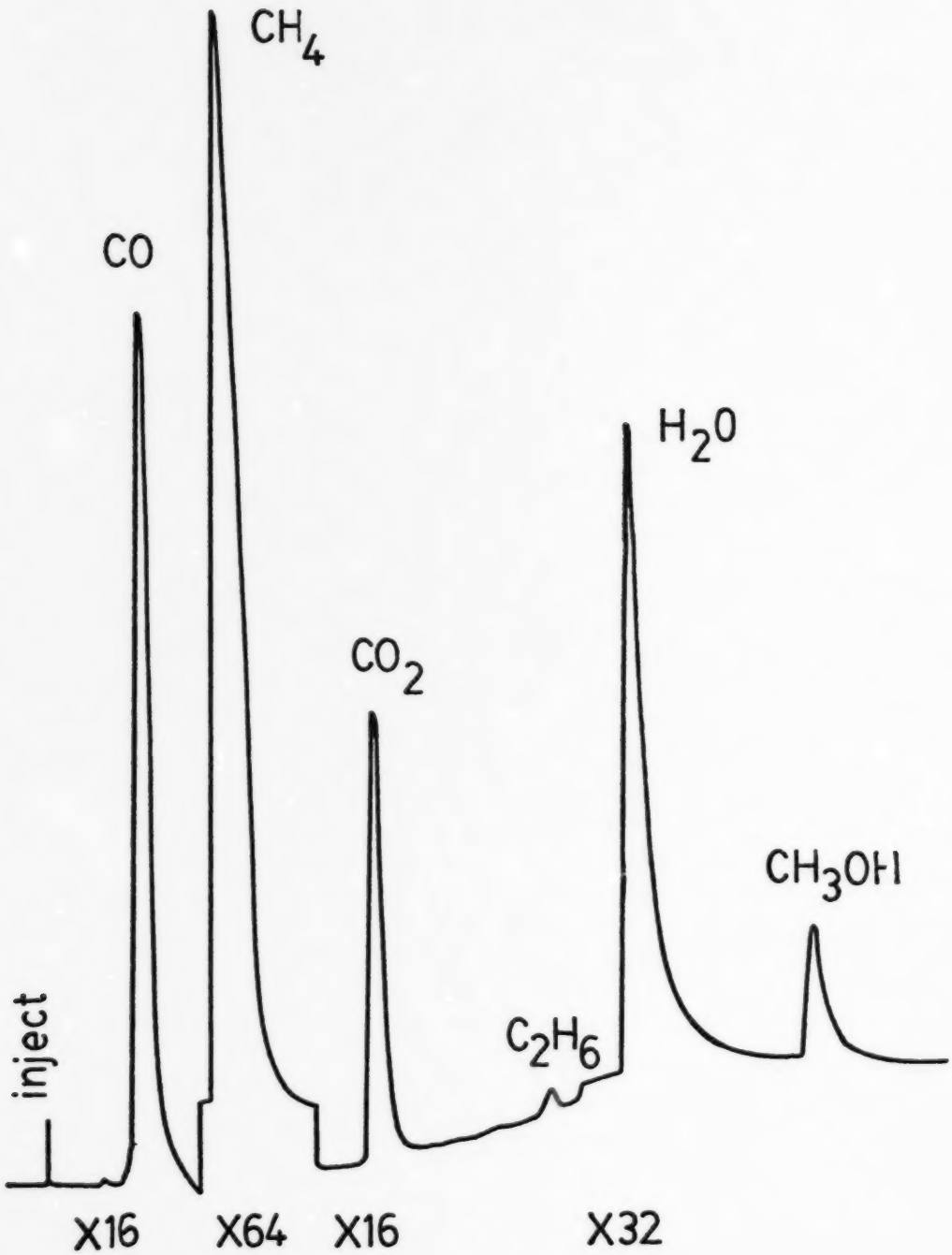


Figure 8. Reaction Chromatogram (i) Temp. program initial 30°C hold 3 min, rise 40°C / min to 175°C final. Column ≡ 10% NPGS / firebrick. (ii) Reactor conditions: Temp. 450°C, Press. 50 atm, Flow Rate-10s(reac.vol). CH_4 / O_2 5:1.

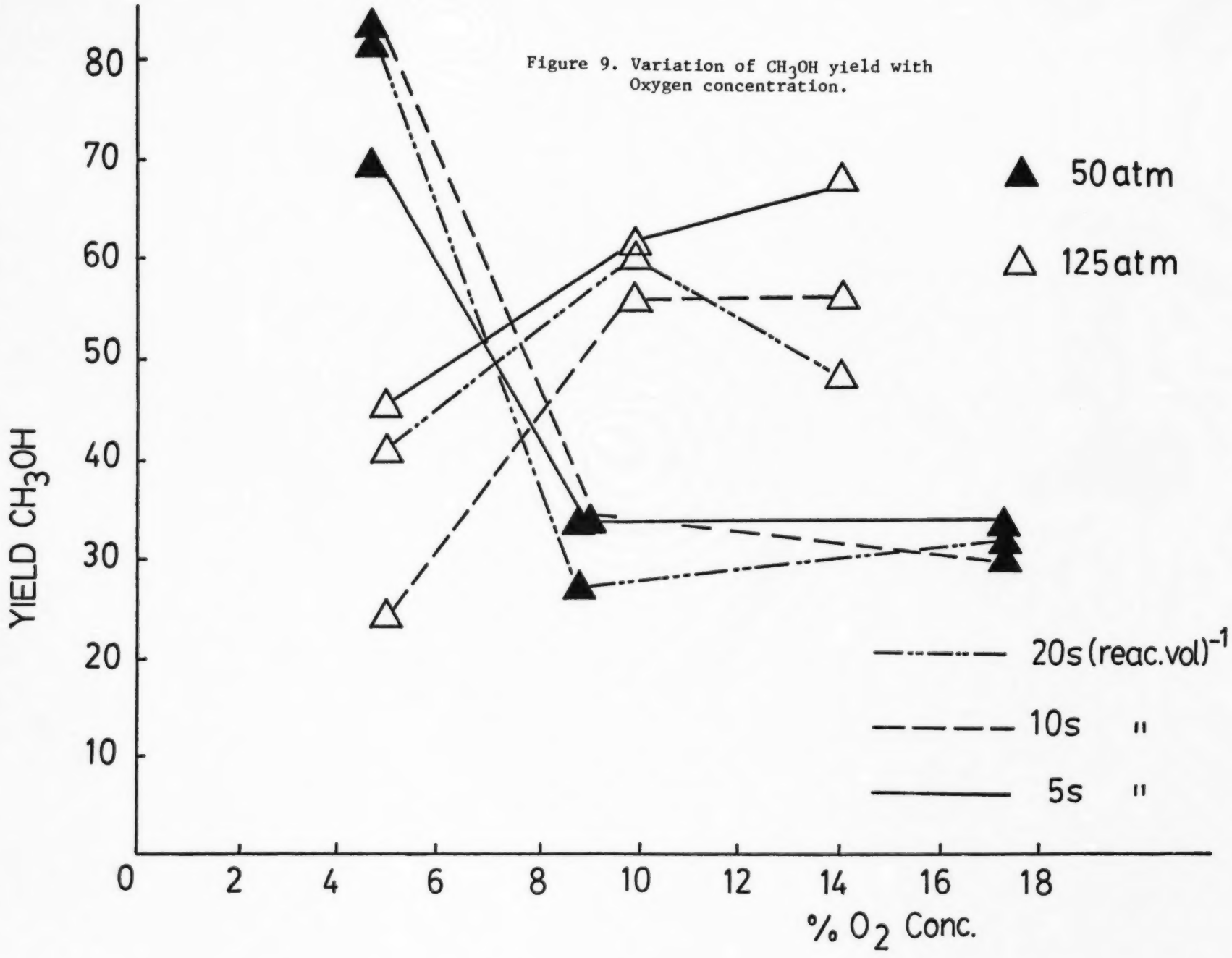


Figure 9. Variation of CH_3OH yield with Oxygen concentration.

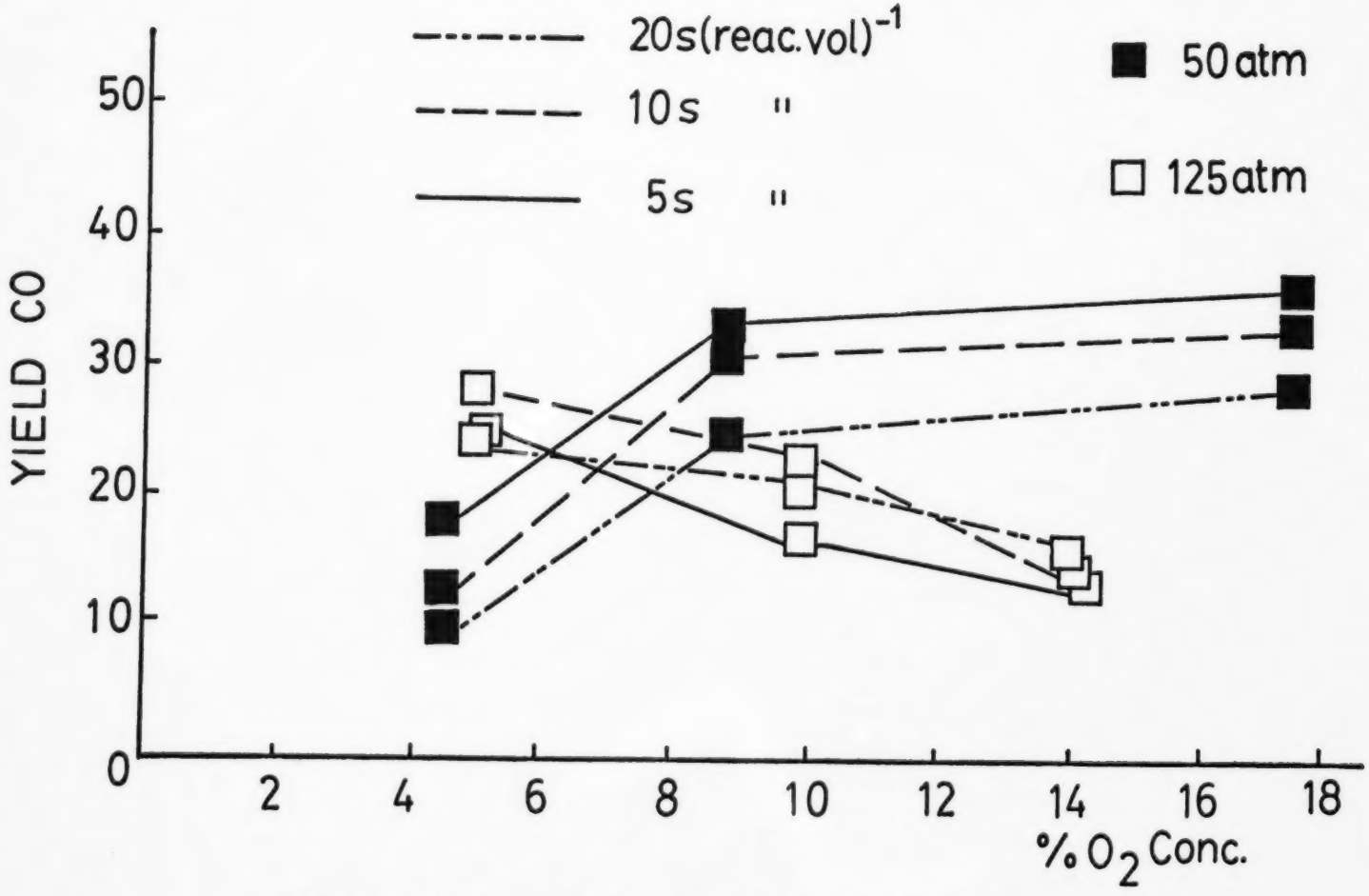


Figure 10. Variation of CO yield with Oxygen concentration.

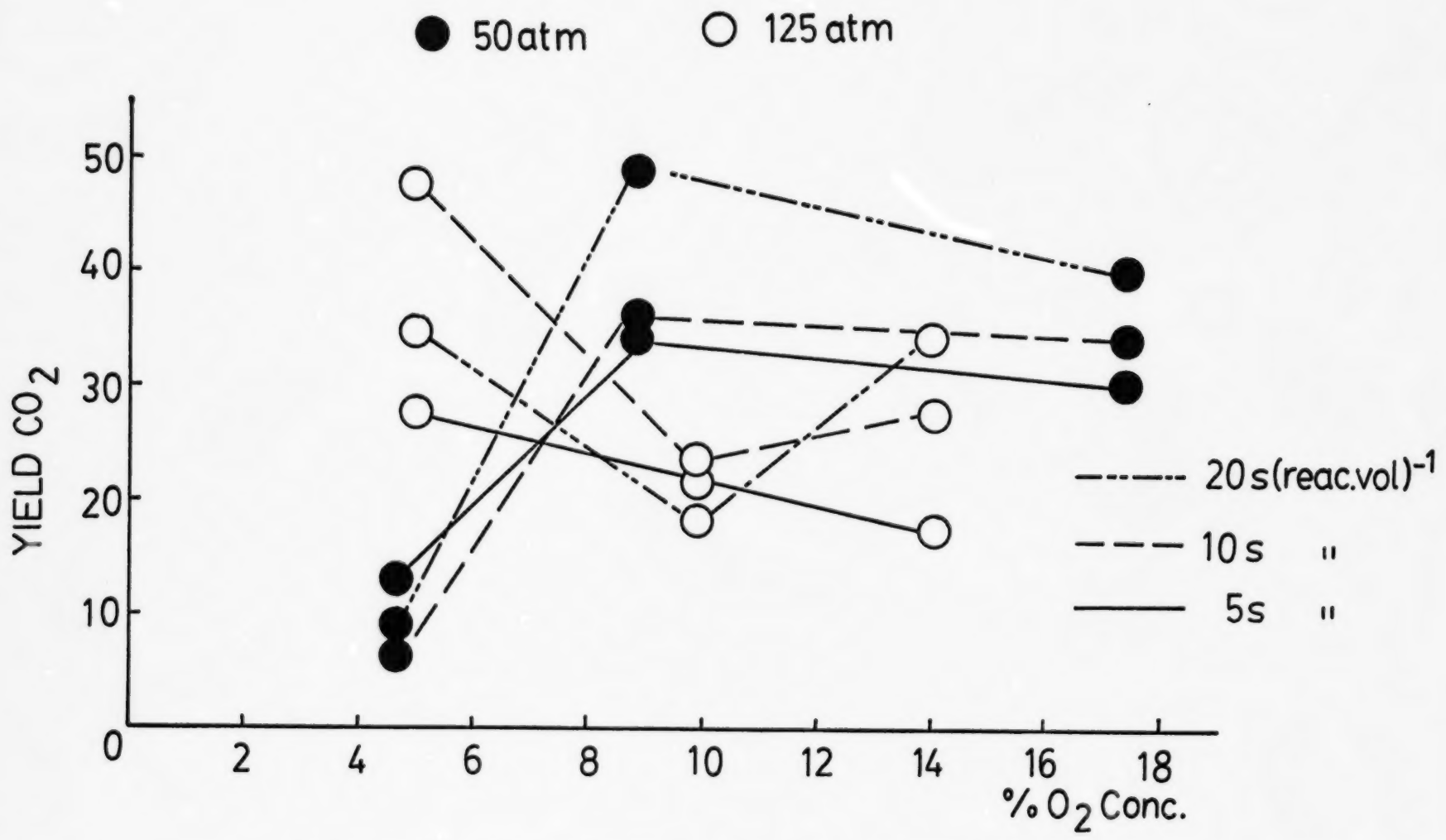


Figure 11. Variation of CO_2 yield with Oxygen concentration.

Figure 12. Variation of CH_3OH yield with flow rate.

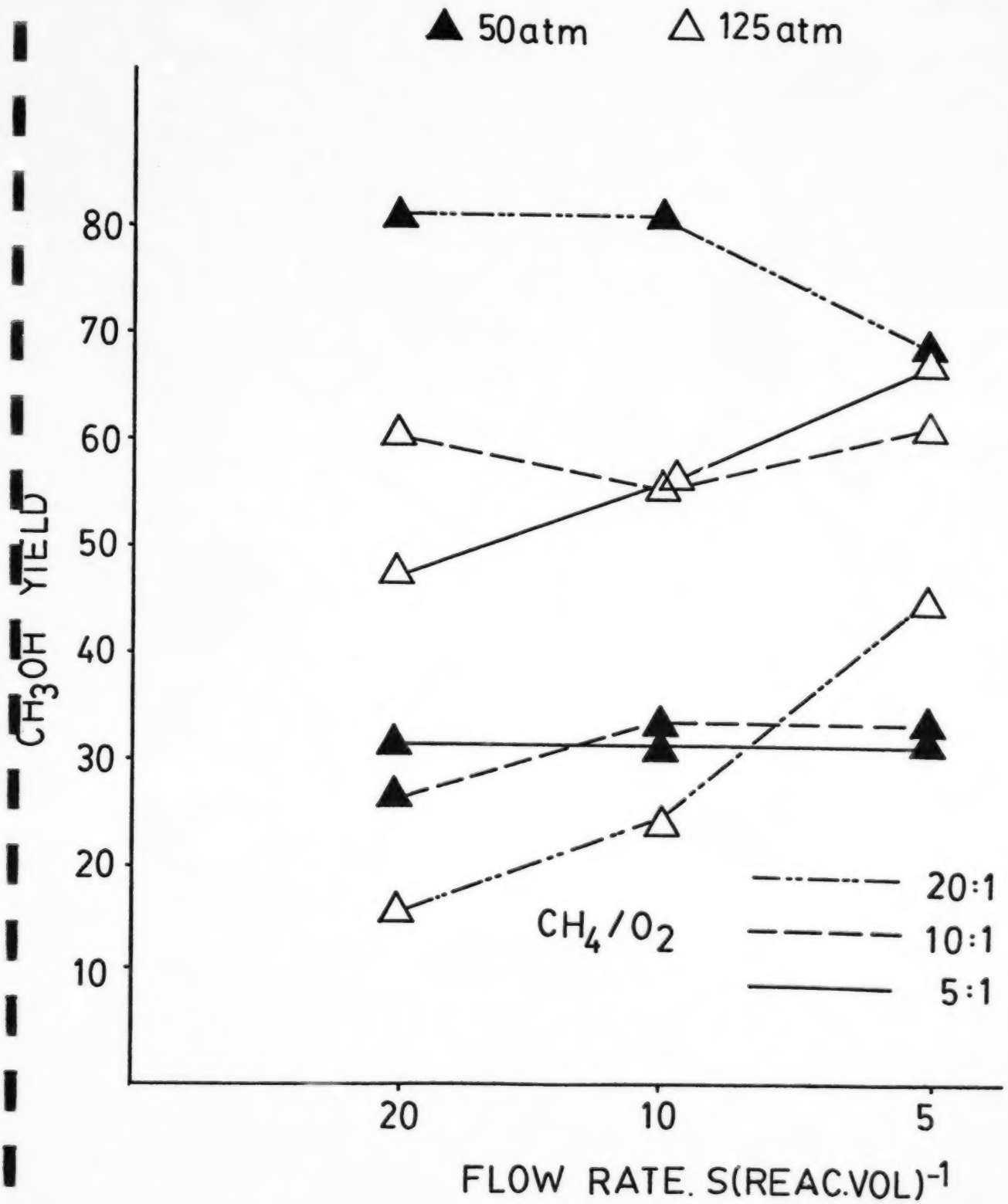
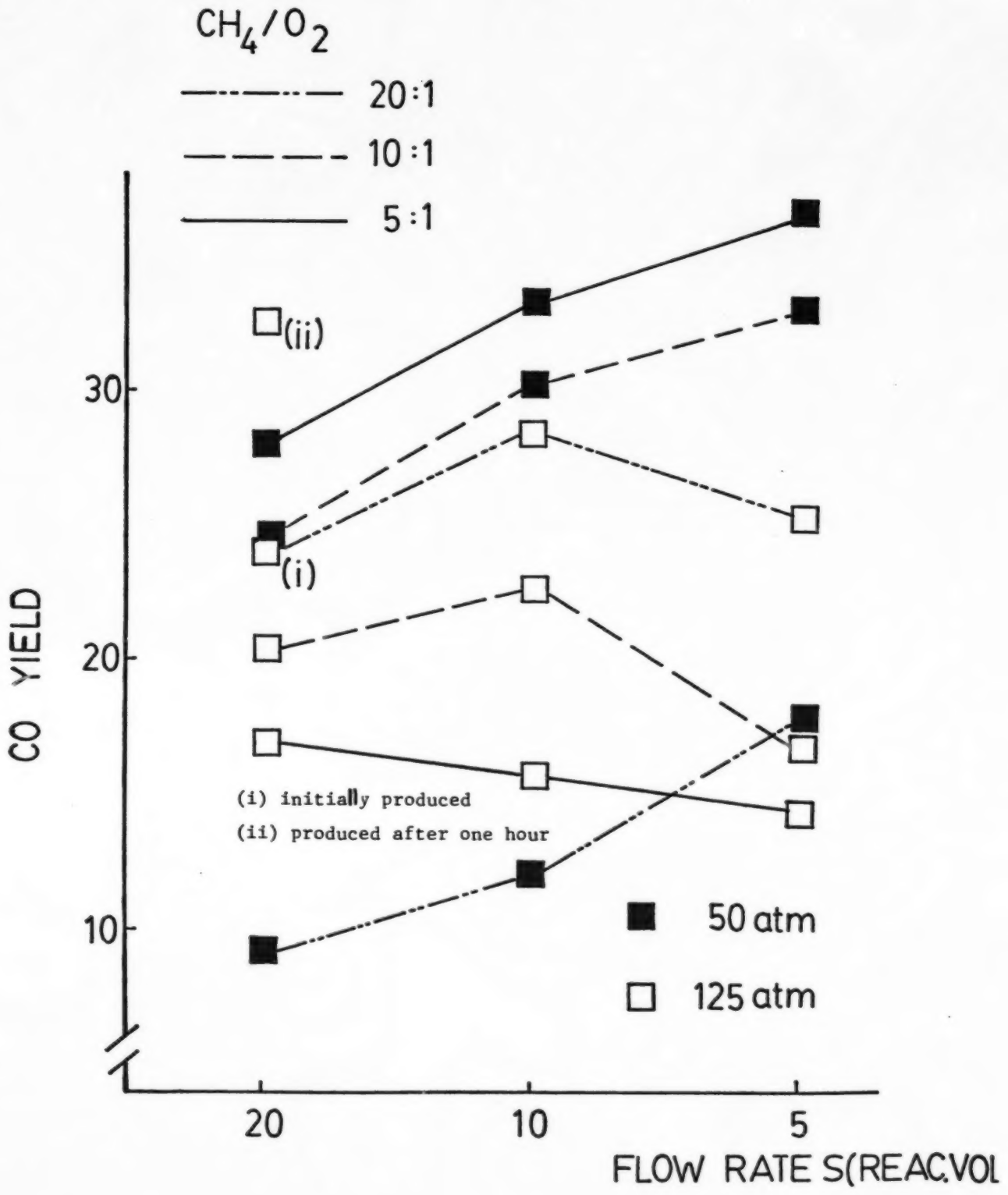
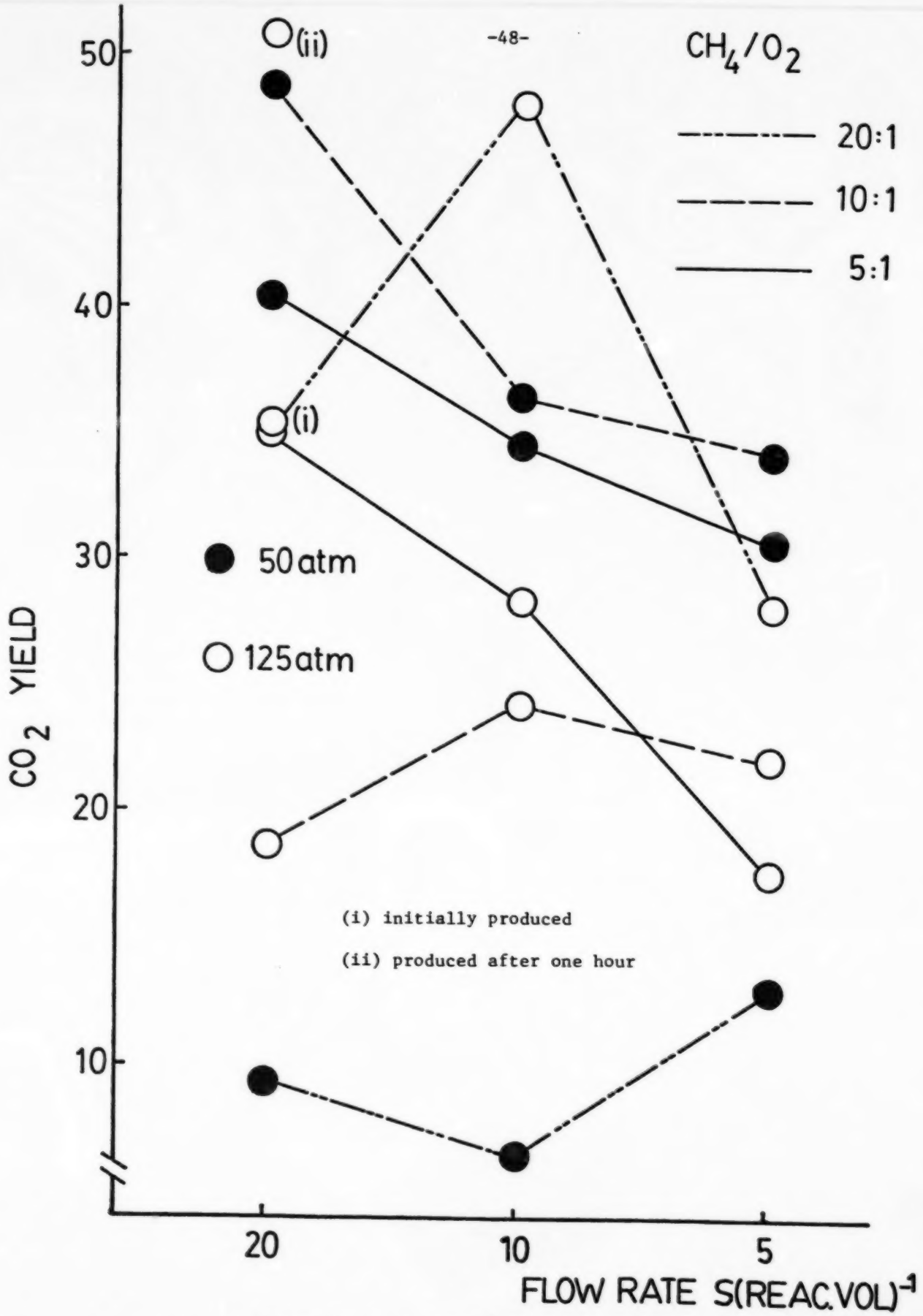


Figure 13. Variation of CO yield with flow rate.

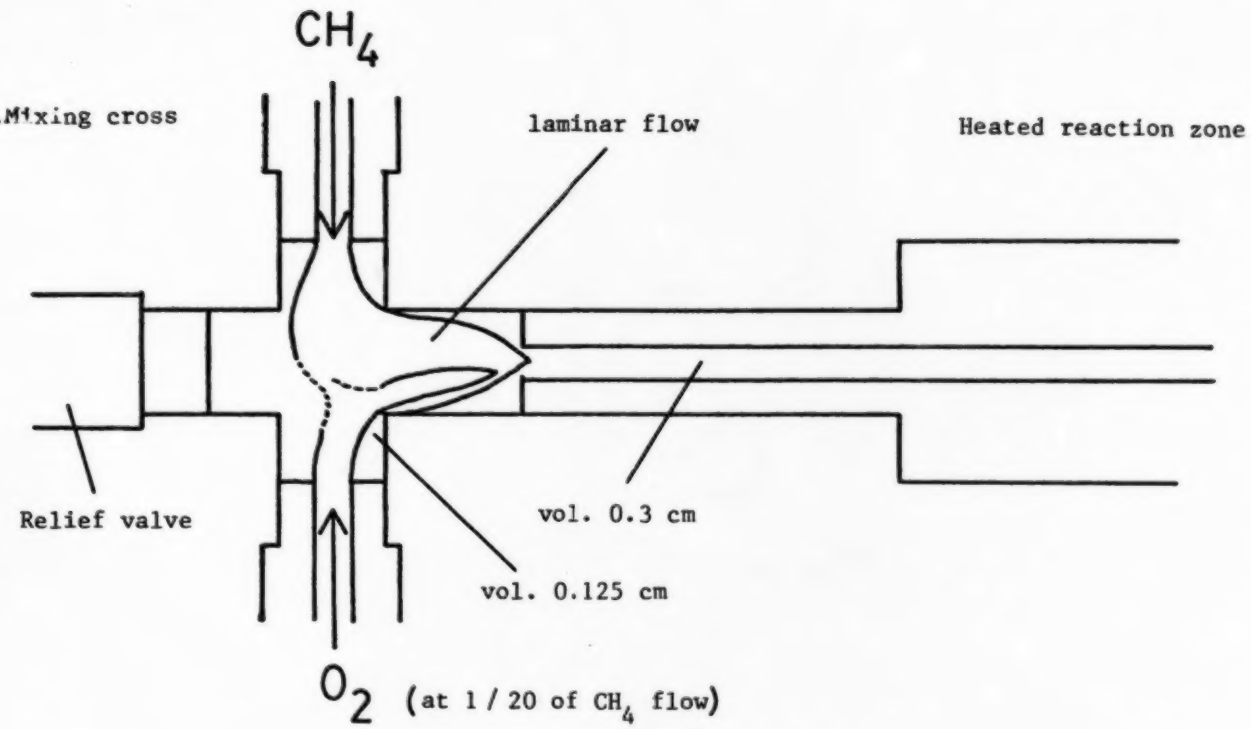




(i) initially produced

(ii) produced after one hour

Figure 14. Variation of CO_2 yield with flow rate.



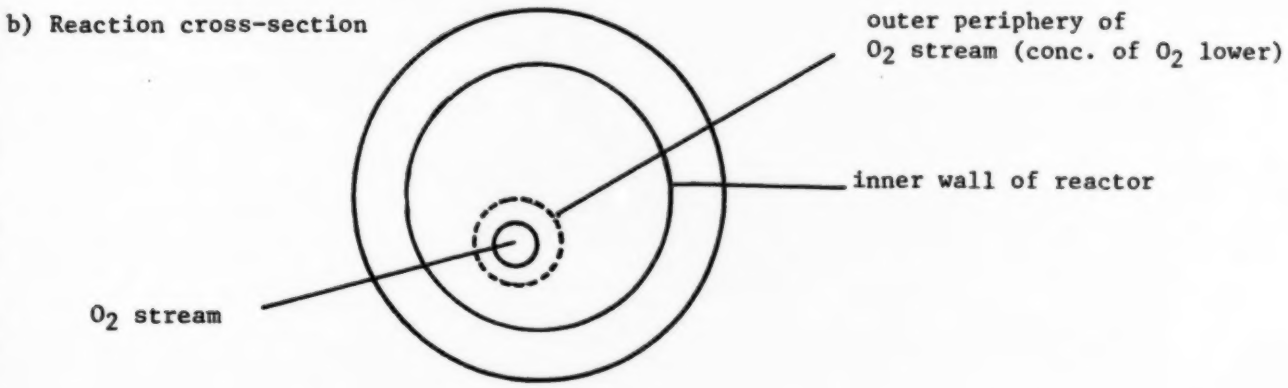


Figure 15. Shematic represention of CH_4 and O_2 in Mixing cross.

APPENDIX A

Table 1A. Reaction Product Analysis - Monoflow System

Pressure = 50 atm, Temperature = 450°C, CH_4/O_2 = 20:1

Run 3 Flow Rate = 20s (reac. vol)$^{-1}$

Compound	O_2	CO	CH_4	CO_2	H_2O	CH_3OH
%total	1.04	1.11	77.46	1.17	9.43	9.78
%C in		1.23	86.53	1.30		10.92
%C burnt		9.20±0.6		9.70±2.4		81.09±4.0

Run 4 Flow Rate = 10s (reac. vol)$^{-1}$

Compound	O_2	CO	CH_4	CO_2	H_2O	CH_3OH
%total	1.15	1.43	72.87	0.77	14.10	9.70
%C in		1.69	85.96	0.91		11.43
%C burnt		12.05		6.51		81.43

Run 5 Flow Rate = 5s (reac. vol)$^{-1}$

Compound	O_2	CO	CH_4	CO_2	H_2O	CH_3OH
%total	1.20	1.94	73.60	1.57	14.3	7.50
%C in		2.29	86.98	1.85		8.86
%C burnt		17.76±0.52		14.25±0.94		68.11±1.47

Table 2A. Pressure = 50 atm, Temperature = 450°C, CH_4/O_2 = 10.4:1

Run 6 Flow Rate = 20s (reac. vol)$^{-1}$

Compound	O_2	OC	CH_4	CO_2	H_2O	CH_3OH
%total 10	0.95	3.46	57.83	6.82	27.13	3.73
%C in 90		4.61	80.03	9.52		5.84
%C burnt		24.74		48.95		26.67

Run 7 Flow Rate = 5s (reac. vol)$^{-1}$

%total	0.75	4.58	49.61	4.74	35.75	4.53
%C in		7.22	62.21	7.49		7.15
%C burnt		33.0		34.2		33.2

Run 8 Flow rate = 10s (reac. vol)$^{-1}$

%total	0.82	4.20	50.26	5.13	34.8	4.67
%C in		6.62	78.01	8.01		7.36
%C burnt		30.4		36.4		33.2

Table 3. Pressure 50 atm, Temperature = 450°C, CH_4/O_2 = 4.76:1

Run 9 Flow rate = 10s (reac. vol)$^{-1}$

%total	trace	5.22	54.67	5.35	29.75	4.97
%C in		7.41	77.84	7.66		7.09
%C burnt		33.4		54.6		31.19

Run 10 Flow rate = 5s (reac. vol)$^{-1}$

%total	trace	5.15	52.67	4.29	33.26	4.59
%C in		7.72	78.93	6.44		6.90
%C burnt		36.7		30.6		32.7

Run 11 Flow rate = 20s (reac. vol)$^{-1}$

%total	trace	4.56	59.44	6.59	25.92	5.13
%C in		6.02	78.42	8.70		6.30
%C burnt		28.0		40.4		31.6

Table 4A. Pressure = 125 atm, Temperature = 450°C, CH_4/O_2 = 9.1:1

Run 12 Flow rate = 20s (reac. vol)$^{-1}$ [23-24]*

Compound	O_2	CO	CO_4	CO_2	H_2O	CH_3OH
%total	-	2.84	69.85	2.59	16.21	8.47
%C in		3.39	83.30	3.10	-	10.17
%C burnt		20.58±2.1	-	18.72±1.5	-	60.67±3.3

Run 13 Flow rate = 10s (reac. vol)$^{-1}$ [13.1-11.9]

%total	-	2.40	78.82	2.64	10.10	6.12
%C in		2.82	87.68	2.94	-	6.81
%C burnt		22.72±2.4	-	24.06±2.6	-	55.6±3.8

Run 14 Flow rate = 5s (reac. vol)$^{-1}$ [4.5-5.1]

%total	-	2.27	75.20	3.00	11.20	8.31
%C in		2.50	84.66	3.39		9.37
%C burnt		16.75±1.1	-	22.12±0.88	-	61.11±1.24

*true flow in s(reac. vol.)$^{-1}$ at NTP.

Table 5A. Pressure = 125 atm, Temperature = 450°C, CH_4/O_2 = 6.2:1

Run 15 Flow rate = 10s (reac. vol)$^{-1}$ [13-11.3]

Compound	O_2	CO	CH_4	CO_2	H_2O	CH_3OH
%total	-	2.87	64.85	5.16	16.60	10.51
%C in		3.43	77.64	6.18	-	12.73
%C burnt		15.74±3.2	-	28.30±5.2	-	56.0±8.2
*C/N_2		1.41	32.10	2.55	-	5.40
*O_2/N_2		0.70	-	2.55	4.5	2.70

*See carbon and oxygen balance, Tables 1 & 2.

Run 16 Flow rate = 5s (reac. vol)$^{-1}$ [4.5-4.2]

%total	-	2.50	51.62	3.06	30.80	12.02
%C in		3.60	74.58	4.42	-	17.38
%C burnt		14.21±2.1	-	17.50±2.0	-	68.21±3.7
C/N_2		1.60	33.26	1.97	-	7.82
O_2/N_2		3.18	-	1.97	10.05	3.91

Run 17 Flow rate = 20s (reac. vol)$^{-1}$ [21.3-20]

%total	-	2.73	65.57	5.63	17.02	7.94
%C in		3.37	79.92	6.89	-	9.82
%C burnt		16.92±2.3	-	34.89±4.6	-	48.21±6.0
C/N_2		1.37±0.24	32.41±1.30	2.81±0.2	-	4.04±1.2
O_2/N_2		0.68±0.12	-	2.81±0.2	4.74±2.4	2.02±0.6

Table 6A. Pressure = 125 atm Temperature = 450°C CH_4/O_2 = 18.7:1

Run 18(i) Flow = 20s (reac. vol)$^{-1}$ [18.2-20.8]

Compound	O_2	CO	CH_4	CO_2	H_2O	CH_3OH
%total	-	1.19	90.5	1.78	4.39	2.08
%C in		1.25	94.65	1.87	-	2.20
%C burnt		24.08±3.3	-	35.31±2.0	-	40.59±4.8
C/N_2		1.14	90.10	1.70	-	1.94
O_2/N_2		0.57	-	0.85	2.11	0.97

Run 18(ii)

%total	-	1.20	94.61	1.93	1.63	0.63
%C in		1.23	96.17	1.97	-	-
%C burnt		32.67	-	51.35	-	15.97
C/N_2		1.20	87.05	1.78	-	0.53
O_2/N_2		0.60	-	1.78	0.75	0.26

Run 19 Flow rate = 10s (reac. vol)$^{-1}$ [9.3]

%total	-	1.27	93.67	1.91	1.80	0.90
%C in		1.30	96.61	1.94	-	0.92
%C burnt		28.57	-	48.13	-	24.33
C/N_2		1.22	89.0	1.85	-	0.86
O_2/N_2		0.61	-	1.85	0.87	0.43

Run 20 Flow rate = 5s (reac. vol)$^{-1}$ [5.1-4.8]

%total	-	1.29	91.08	1.47	3.77	2.37
%C in		1.34	94.65	1.52	-	2.46
%C burnt		25.39±2.84	-	28.08±6.3	-	45.0±4.7
C/N_2		1.40	98.76	1.60	-	2.58
O_2/N_2		0.70	-	1.60	2.04	1.29

Table 6A...cont'd...

Run 20(a) Flow rate = 3.4s (reac. vol)$^{-1}$

%total	-	1.33	89.45	1.12	3.9	2.37
%C in		1.39	93.25	1.20	-	4.15
%C burnt		20.56	-	17.81	-	61.61
O/N_2		1.45	98.95	1.27	-	4.41
O_2/N_2		0.72		1.27	2.14	2.20

Run 20(b) Flow rate = 4.24s (reac. vol)$^{-1}$

%total	-	1.41	86.34	1.42	7.17	3.63
%C in		1.52	93.03	1.53	-	3.92
%C burnt		21.88	-	21.83	-	56.27
C/N_2		1.42	87.30	1.44	-	3.68
O_2/N_2		0.71	-	0.72	3.65	1.84